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AFRPL-TR-67-134

(Unclassified Title)

**FINAL REPORT,  
INVESTIGATION OF LIQUID-METAL HYDRIDES**

L. R. Grant  
F. C. Gunderloy, Jr.  
R. I. Wagner  
E. F. Witucki

Rocketdyne, A Division of North American Aviation, Inc.  
6633 Canoga Avenue, Canoga Park, California

**TECHNICAL REPORT AFRPL-TR-67-134**

April 1967

Group 4  
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## FOREWORD

This final report is submitted in compliance with Contract AFO4(611)-11532, Part I, Paragraph B.1, Line Items 6 and 7. This research program was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards Air Force Base, California. Messrs. G. A. Beale and R. A. Biggers of RPCL served as project monitors.

The program was conducted in the Chemical and Materials Sciences Department (Manager, Dr. J. Silverman), Rocketdyne Research Division. Drs. J. Silverman and Emil A. Lawton (Manager, Synthetic and Propellant Chemistry) served as Program Managers. Personnel contributing to the program were:

Dr. Louis R. Grant (Responsible Scientist)  
Dr. Frank C. Gunderloy, Jr. (part-time)  
Dr. Ross I. Wagner  
Mr. Edward F. Witucki (part-time)

This report has been assigned the Rocketdyne report number R-7002.

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF  
Chief, Propellant Division

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## CONFIDENTIAL ABSTRACT

- (C) Studies of liquid beryllium hydride synthesis have resulted in a number of new species with theoretical specific impulses approaching 330 seconds and further defined the most promising classes of this type of high-energy fuel. In general, it appears that terminators derived from higher borane fragments (e.g.,  $B_3H_7$ ) are more advantageous than simple  $BH_3$  terminators. Liquids with  $B_3H_7$  terminators exhibit high theoretical impulse and satisfactory fluidity, and unlike many  $BH_3$ -terminated liquids, are not subject to reversible dissociation.
- (C) The bulk of this investigation was concerned with the preparation of borane-terminated beryllium hydride (BTBH) liquids from the reaction of  $B_4H_{10}$  with beryllium alkyls and alkylberyllium hydrides. The nature of the reaction products was dependent upon the experimental conditions. The use of a  $B_4H_{10}/Be(CH_3)_2$  mole ratio of 0.5 and an extended reaction time yielded the best product, a liquid analyzing as  $B_3H_7(CH_3BeH)_2BeH_2BH_3$  (specific impulse, 329 seconds with  $H_2O_2$ ).
- (C) The use of  $B_2H_6/B_4H_{10}$  mixtures simplified the complex reactions involving pure  $B_4H_{10}$  and solid beryllium compounds. Such mixtures increased the liquefaction rates of the beryllium compounds and also resulted in a significant decrease in the amount of  $B_4H_{10}$  decomposition during its reactions.
- (C) Ethyl-substituted BTBH liquids were synthesized. The compound  $B_3H_7 - (C_2H_5BeH) BeH_2BH_3$  (specific impulse, 326 seconds) remained fluid at  $-40^\circ C$ .
- (C) Conditions for the quantitative reaction of  $Al(CH_3)_3$  and Beane were established for the preparation of alane-terminated beryllium hydride (ATBH) liquids. The displacement of the alane terminators from ATBH liquids by  $B_2H_6$ ,  $B_4H_{10}$ , or  $Be(BH_4)_2$  demonstrated the feasibility of employing ATBH materials as precursors for BTBH liquids.

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## INTRODUCTION

- (C) The Investigation of Liquid-Metal Hydrides is the unclassified title of work performed at Rocketdyne on the preparation of a new class of storable liquid propellants containing beryllium and hydrogen. Because beryllium hydride is the best of the solid or hybrid propellant fuels in terms of theoretical specific impulse, particularly if calculations are carried out with  $H_2O_2$  as the oxidizer, a great deal of interest has been generated in attempting to develop related storable liquid propellant systems.
- (C) The new class of fuels under investigation at Rocketdyne utilizes the ability of borane and alane moieties to terminate polymeric beryllium materials, and as a consequence yield liquid beryllium complexes. For this reason, these materials are referred to as borane- and alane-terminated beryllium hydride fuels.
- (C) The previous research effort, conducted under Contract AF04(611)-8550, demonstrated the feasibility of synthesizing borane-terminated beryllium hydride (BTHH) liquid fuels from reactions of known beryllium compounds and boron hydrides and/or their derivatives (Ref. 1). The primary goals of the present program were to prepare new and/or improved borane- and alane-terminated beryllium hydride liquid fuels with good liquid properties, thermal stability, and theoretical specific impulse. Because of the demonstrated greater thermal stability of the first triborane-terminated materials (Ref. 2) and their generally good liquid viscosities, much of the effort reported herein was concerned with the reactions of  $B_4H_{10}$ , a source of triborane groups, and polymeric beryllium compounds. As a consequence of these studies, a number of new BTHH liquids, having calculated specific impulse values approaching 330 seconds, were prepared. The best of these, in terms of specific impulse, was a compound analyzing as  $B_3H_7 - (CH_3BeH)_2BeH_2BH_3$  (specific impulse, 329 seconds).
- (C) The reaction studies have also provided further definition of both the structural features and the chemical routes that must be pursued in the future development of liquid beryllium hydride. In general, it appears that the use of higher borane terminators, such as  $B_3H_7$ , leads to good

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fluidity and high specific impulse, but that further increases in  $\text{BeH}_2$  content must be achieved in a controllable fashion to greatly exceed the 330-second specific impulse level.

- (U) The synthetic experimental effort of this program was divided informally into three phases: Phase I, Preparation and Modification Studies; Phase II, Preliminary Characterization of Liquid Products; and Phase III, Tailoring of BTHH Fuels. Because of the interrelationship of the work performed under these phases, the results are reported in a combined fashion.

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## PERFORMANCE OF LIQUID BERYLLIUM FUELS

- (C) The theoretical specific impulse values of some postulated liquid beryllium fuels are compared with that of  $\text{BeH}_2$  in Table 1, and those of actual liquids prepared under this contract are presented in Table 2. The heats of formation presented for the compounds in Tables 1 and 2 were derived from bond energies calculated from the experimental heats of formation of beryllium hydride (Ref. 3), beryllium borohydride (Ref. 4), and beryllium alkyls (Ref. 5). All other bond energy values were excerpted from Ref. 6.
- (C) In Table 2, both ethyl- and methyl-substituted BTEH liquids are listed, and both borane ( $\text{BH}_3$ ) and triborane ( $\text{B}_3\text{H}_7$ ) terminators or their alkyl derivatives are presented. Based on the data presented in Tables 1 and 2, the following facts are noteworthy:
1. Large changes in heats of formation do not appreciably affect performance unless the compound in question contains very few alkyl groups.
  2. Alkyl substitution on the boron terminator is more detrimental to the performance than alkyl substitution on the beryllium.
  3. Although the relative amount of hydrogen per unit weight is greater in the  $\text{BH}_3$  group than in the  $\text{B}_3\text{H}_7$  moiety, liquids can still be prepared having a calculated specific impulse closely approaching 330 seconds.
  4. One ethyl group is better for performance than two methyl groups.

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TABLE 1

THEORETICAL PERFORMANCE OF SOME POSTULATED  
BERYLLIUM COMPOUNDS

Compound	Estimated Heat of Formation, kcal/mole	Specific Impulse with $H_2O_2$ (shifting, 1000 - 14.7 psia), seconds
$(BeH_2)_n$	-5.6	357
$H_3B(CH_3BeH)(BeH_2)_9BH_3$	-82	352
$H_3B(CH_3BeH)(BeH_2)_3BH_3$	-45 (-11)	342 (351)
$H_3B(BeH_2)_2(CH_3BeH)_2BH_3$	-47 (-12)	338 (341)
$(CH_3BH_2)_2(BeH_2)_4$	-70 (-37)	333 (336)
$H_3B(C_2H_5BeH)_3(BeH_2)_6BH_3$	-85	333

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TABLE 2

THEORETICAL PERFORMANCE OF SOME KNOWN  
BERYLLIUM LIQUIDS

Compound	Estimated Heat of Formation, kcal/mole	Specific Impulse With $H_2O_2$ (shifting 1000 → 14.7 psia), seconds
$B_3H_7(CH_3BeH)_2(BeH_2)BH_3$	-20	329
$B_3H_7(CH_3BeH)_3(BeH_2)BH_3$	-50	326
$B_3H_7(C_2H_5BeH)(BeH_2)BH_3$	-10	326
$B_3H_7(CH_3BeH)_2BH_3$	-15	320
$C_2H_5BH_2(C_2H_5BeH)(BeH_2)BH_3$	-20	311
$(B_3H_7)_2(C_2H_5BeH)_4(BeH_2)$	-20	315
$(B_3H_7)_2(C_2H_5BeH)_3(BeH_2)$	-10	317
$(CH_3B_3H_6)_2(CH_3BeH)_3(BeH_2)$	-35	321

**DISCUSSION AND RESULTS**

**PREPARATION OF THE BTEH LIQUIDS**

- (C) Reactions involving the agents shown in Table 3 have been used to convert known beryllium-containing solids to BTEH liquids.

**TABLE 3**

**COMPONENTS OF BTEH LIQUIDS**

Beryllium Compounds	Borane Agents	Beryllium-Boron Agents
$[(CH_3)_2Be]_n$	$B_4H_{10}$	$Be(BH_4)_2$
$[(C_2H_5)_2Be]_n$	$B_2H_6$	$(CH_3BeBH_4)_2$
$[(C_2H_5)_2Be \cdot C_2H_5BeH]_n$	alkyldiboranes	
$[CH_3BeH]_n$		
$(BeH_2)_n$		

These reactions are quite complex, in most instances, and involve several steps (not necessarily in the sequence presented):

1. Direct termination of a polymeric beryllium compound with a borane agent, or a beryllium-boron agent.
2. Chain scission of the polymeric beryllium compound followed by termination with a borane moiety.
3. Hydriding of the beryllium-alkyl bond by the borane agent with the concomitant formation of a boron-alkyl species.

- (C) The simplest of the BTEH liquids to prepare are those involving dimethylberyllium and  $Be(BH_4)_2$  or  $(CH_3BeBH_4)_2$ . However, the calculated specific impulse (310 to 315 seconds) of these materials indicated they were

unsatisfactory propellants. The thermal stability of a few  $\text{BH}_3$ -terminated liquids have been examined (Ref. 2), although no systematic investigation was conducted. The liquids studied were chosen on the basis of availability and were tested for their stability as media for  $(\text{BeH}_2)_x$  gels. In all cases, some gas was evolved at 160 F which proved to be primarily  $\text{B}(\text{CH}_3)_3$ . This borane derivative cannot serve as a terminator and, consequently, when it is formed as a result of internal rearrangement, it is readily evolved. The compound  $(\text{CH}_3\text{B}_3\text{H}_6)_2(\text{CH}_3\text{BeH})_3\text{BeH}_2$ , however, was much more stable, even though a  $\text{B}-\text{CH}_3$  bond was already present in the material. On this basis,  $\text{B}_3\text{H}_7$  termination appeared to be a logical approach to the preparation of thermally stable BTBH liquids.

- (U) A summary of the  $\text{B}_4\text{H}_{10}$  reactions investigated is presented in Table 4. A more detailed description of the reactions is presented in the following paragraphs.

$\text{B}_4\text{H}_{10}/\text{Be}(\text{CH}_3)_2$  Reaction System

- (C) The reaction of  $\text{B}_4\text{H}_{10}$  and  $\text{Be}(\text{CH}_3)_2$  was found to yield liquids of high theoretical specific impulse (Table 2). However, the composition of the products was dependent, to a large degree, upon the experimental conditions used (Table 4). The following variables were investigated in an attempt to establish those conditions best suited for the preparation of a BTBH liquid with a calculated specific impulse  $\geq 330$  seconds.

1. Relationship of the physical state of  $\text{B}_4\text{H}_{10}$  to its reactivity
2. Mole ratios of the reactants
3. Reaction time
4. Effect of  $\text{B}_2\text{H}_6$  as an initiating agent for  $\text{Be}(\text{CH}_3)_2$  liquefaction

Throughout these studies, temperatures were maintained at ambient or below to hold the decomposition of  $\text{B}_4\text{H}_{10}$  (one of the unstable boranes) to a minimum. However, such decomposition was not completely avoidable.

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TABLE 4

SUMMARY OF  $B_4H_{10}/Be(CH_3)_2$  REACTIONS

Experiment No.	$B_4H_{10}/Be(CH_3)_2$ Mole Ratio	Reaction Conditions	Comments
1	1.0	Liquid $B_4H_{10}$ at ambient temperature	No significant amounts of liquid beryllium products were formed. The principal beryllium-containing product was $BeH_2$ .
2	1.0	$B_4H_{10}$ vapor at ambient temperature	Liquefaction of the $Be(CH_3)_2$ occurred after 26 hours. The liquid analyzed as $[(CH_3)_3BH]_2(BeH_2)_2(CH_3BeH)_2$ .
3	2.0	$B_4H_{10}$ vapor at ambient temperature	The beryllium alkyl was converted to liquid products in less than 20 hours. After 23 hours, solids precipitated from the reaction mixture, and continued to do so until the reaction was stopped after 29 hours. Analyses of this solid product were not performed.
4	1.0	$B_4H_{10}$ vapor at ambient temperature	Formation of liquid products required 25 hours. Further reaction caused complete solidification of the liquid product after a total reaction time of 97 hours. The product was not analyzed.
5	0.5	$B_4H_{10}$ added incrementally at ambient temperature	Conversion of the $Be(CH_3)_2$ to liquid products was complete after 120 hours. A liquid analyzing as $B_3H_7(CH_3BeH)_2BeH_2BH_3$ was isolated.
6	0.5	$B_4H_{10}$ added incrementally at ambient temperature	After 120 hours, a liquid was isolated which analyzed as $B_3H_7(CH_3BeH)_2BeH_2CH_3$ .

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- (C) Physical State of  $B_4H_{10}$  and Its Reactivity. The products of the  $Be(CH_3)_2/B_4H_{10}$  reaction are quite dependent upon the physical state of the  $B_4H_{10}$ . The reaction of equimolar amounts of  $Be(CH_3)_2$  and liquid  $B_4H_{10}$ , a condition under which hydriding of the beryllium alkyl was expected to be extensive, never yielded a one-phase system. Instead, the slurry of  $Be(CH_3)_2$  and liquid  $B_4H_{10}$  remained colorless, thickened to a maximum after 6 hours, and subsequently became more fluid than the initial mixture before quenching after 29.5 hours. The solid present at the end of this time was the principal beryllium-containing product and was identified as impure  $BeH_2$ .
- (C) The reaction of equimolar amounts of  $Be(CH_3)_2$  and  $B_4H_{10}$  vapor, however, caused complete liquefaction of the beryllium alkyl after approximately 26 hours. The liquid product, the composition of which corresponded to the empirical formula  $[(CH_3)_3B_3H_4]_2(CH_3BeH)_2(BeH_2)_2$  was a mobile liquid, but its high methyl group content negated its importance as a high-energy fuel.
- (C) In the presence of liquid  $B_4H_{10}$ , the hydriding of  $Be(CH_3)_2$  to  $BeH_2$  is quite rapid. The failure to obtain appreciable quantities of BTEH liquids when liquid  $B_4H_{10}$  was used as the reactant was attributed to the more favorable formation of solid  $BeH_2$  in this reaction medium. Under comparable experimental conditions, however, the  $B_4H_{10}$  vapor-phase reaction, being a solid/gas reaction, was a much slower reaction and the extent of hydriding of the  $Be(CH_3)_2$  was much less. This reasoning is supported by the nature of the products obtained.
- (C) Mole Ratios of  $B_4H_{10}$  and  $Be(CH_3)_2$ . Although low  $B_4H_{10}/Be(CH_3)_2$  mole ratios would be expected to yield liquids with the higher degrees of polymerization, these conditions would also most likely result in slower  $Be(CH_3)_2$  liquefaction rates, and less hydriding of the beryllium alkyl. Therefore, it was desirable to determine if by altering the mole ratios of the reactants, a compromise could be reached between reaction rates, hydriding, and apparent degrees of polymerization of the final liquid product.

(C) Experiments were conducted using  $B_4H_{10}$  (vapor)/ $Be(CH_3)_2$  mole ratios of 0.5, 1.0, and 2.0 to determine the relative rates of  $Be(CH_3)_2$  liquefaction (Table 4). The rate of conversion of  $Be(CH_3)_2$  to liquid products decreased in the order  $2.0 > 1.0 > 0.5$ . A consideration of the instability of  $B_4H_{10}$ , however, suggested that these same results could be explained by assuming that the  $Be(CH_3)_2$  liquefaction was initiated by a disproportionation product of  $B_4H_{10}$ , most likely  $B_2H_6$ , rather than  $B_4H_{10}$  itself. Although the total amount of  $B_4H_{10}$  available for reaction differed during these experiments, the experimental conditions (at mole ratios of 1.0 and 2.0) were such that the actual amount of  $B_4H_{10}$  vapor in contact with the  $Be(CH_3)_2$  was identical at any given time. This was the case because the amount of  $B_4H_{10}$  vapor was governed by the vapor pressure of the liquid boron hydride present. The postulate that  $B_2H_6$ , derived from the disproportionation of  $B_4H_{10}$ , was initiating the liquefaction of  $Be(CH_3)_2$  was tested experimentally.

(C) Influence of  $B_2H_6$  on the  $B_4H_{10}/Be(CH_3)_2$  Reaction. The reaction of  $Be(CH_3)_2$  with mixtures of  $B_4H_{10}$  and  $B_2H_6$  (mole ratio  $\sim 4:4:1$ , respectively) resulted in approximately a fourfold decrease in the time required (6 vs 26 hours) for liquefaction of the  $Be(CH_3)_2$  by  $B_4H_{10}$  alone (Table 5). From earlier work on the  $B_2H_6/Be(CH_3)_2$  system (Ref. 1), it is known that the amount of  $B_2H_6$  used was insufficient to cause liquefaction of the beryllium alkyl. Consequently, the increased liquefaction rate observed for the ternary system must be attributed to a reaction involving both  $B_2H_6$  and  $B_4H_{10}$ . However, the liquids isolated from these reactions were found to contain significant amounts of methyl groups.

(C) Decomposition of  $B_4H_{10}$  During Reaction. The preceding discussion has demonstrated some of the difficulties associated with the use of  $B_4H_{10}$  as a liquefying agent for  $Be(CH_3)_2$ , viz:

1. Instability of  $B_4H_{10}$
2. Slow reaction rates

TABLE 5

SUMMARY OF  $B_4H_{10}/B_2H_6/Be(CH_3)_2$  REACTIONS  
(Vapor-Phase Reaction at Ambient Temperature)

Experiment No.	$B_4H_{10}/B_2H_6/Be(CH_3)_2$ Mole Ratio	Comments
1	4.0:1.0:4.2	Liquefaction of the metal alkyl was complete after 6 hours. The reaction time was extended to 8.0 hours, after which time a slightly turbid liquid was formed. By material balance, the average composition of the product was $B_3H_7(CH_3BeH)_2 [(CH_3)_2Be]_3BH_3$ .
2	4.0:1.0:3.8	Conversion of the $Be(CH_3)_2$ to a liquid occurred in 6 hours. No change in the physical state of the reaction mixture was observed after a total reaction time of 7.5 hours. Analyses of the product corresponded to a 39:61 mixture of $B_3H_7(CH_3BeH)_2 [Be(CH_3)_2]_2BH_3$ and $B_3H_7(CH_3BeH)_4CH_3$ .
3	3.9:1.0:3.8	The reaction was run for 15.3 hours. After this time the liquid product had become slightly turbid. By material balance, the average composition of the product was $B_3H_7 [Be(CH_3)_2]_2(CH_3BeH)_2BH_3$ .

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Disproportionation products of  $B_4H_{10}$  other than  $B_2H_6$  are  $B_5H_9$ ,  $B_5H_{11}$ ,  $H_2$ , and nonvolatile  $(BH)_x$  species. These boron hydrides might also react with the beryllium alkyl, and as a result it was necessary to investigate how their formation might be suppressed.

- (C) The use of  $B_2H_6$  to increase the liquefaction rate of  $Be(CH_3)_2$  also served to suppress the disproportionation of  $B_4H_{10}$ . For example, when the stability of a 1:4 mixture of  $B_2H_6$  and  $B_4H_{10}$  was tested for 8 hours at ambient temperature, the  $B_4H_{10}$  was recovered quantitatively. The recovery of  $B_4H_{10}$  from this test was greater than predicted based upon the decomposition of  $B_4H_{10}$  vapor at low pressures (40 millimeters, Ref. 7). It was also observed that 31 percent of the  $B_2H_6$  was not recovered from the stability experiment (conducted at a total pressure of approximately 650 millimeters). Conversion of the more stable boron hydride  $B_2H_6$  to  $B_4H_{10}$ , a known reaction at much higher pressures, must have occurred to replenish any  $B_4H_{10}$  which disproportionated (Eq. 1).



Evidence for this type of reaction was the correspondence of unrecovered  $B_2H_6$  and the  $H_2$  formed during the stability experiment.

- (C) Reaction Time. As a result of the disproportionation of  $B_4H_{10}$ , the reaction time required for the conversion of  $Be(CH_3)_2$  to liquid products decreased with increasing  $B_4H_{10}/Be(CH_3)_2$  mole ratios. When  $B_4H_{10}/Be(CH_3)_2$  mole ratios of  $\geq 1.0$  were used, further hydriding of the liquid products to solids also occurred more rapidly. For example, during an experiment in which the  $B_4H_{10}/Be(CH_3)_2$  mole ratio was 1.0, the beryllium alkyl was completely liquefied after 26 hours at ambient temperature and remained so until the reaction was stopped after 29.5 hours; unreacted  $B_4H_{10}$  (28 percent of the original amount) was present after this time. During a second experiment, using the same mole ratio, solids were obtained when the reaction time was extended to 30 hours. A third experiment, conducted at

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a mole ratio of 2.0, demonstrated that the metal alkyl could be converted into liquid products in 18 hours, after which time solids were rapidly formed.

## Summary of $B_4H_{10}/Be(CH_3)_2$ Reactions

- (C) The best conditions for the preparation of high-energy BTBH liquids appear to be the use of  $B_4H_{10}/Be(CH_3)_2$  mole ratios of  $<1.0$  and long reaction times. The use of long reaction times appears to be necessary for controlled hydriding of the  $Be-CH_3$  bonds. At the same time, however, extended reaction times are apt to yield the greatest amount of  $B_4H_{10}$  decomposition. It is possible that the action of  $B_4H_{10}/B_2H_6$  mixtures on  $Be(CH_3)_2$ , at different mole ratios and increased reaction times, may yield the amount of hydriding desired. However, because other approaches appeared equally promising, this approach was not investigated.

## Conversion of $Be(C_2H_5)_2$ to BTBH Liquids

- (C) Because of the physical state of  $Be(C_2H_5)_2$ , a liquid at ambient temperature, it was anticipated that its reactions with  $B_4H_{10}$  might be faster and less complex than those between  $B_4H_{10}$  and  $Be(CH_3)_2$ . Furthermore, the successful preparation of ethyl-substituted BTBH liquids might result in materials with better physical properties.
- (C) It was demonstrated under Contract AF04(611)-8550 that the viscosity of BTBH liquids having the general formula  $(BH_3)_2[(CH_3)_mBe_{\frac{m+n}{2}}H_n]^x$  increased with the degree of polymerization (x) and the hydrogen content (n), (Ref. 1). As a consequence, those liquids yielding the best calculated specific impulse possessed the highest viscosity, as the examples in Table 6 demonstrate.

TABLE 6

SPECIFIC IMPULSE VALUES AND VISCOSITIES OF SOME BTEH SPECIES

Formula	Specific Impulse (H <sub>2</sub> O <sub>2</sub> ), seconds	Viscosity Similarity
$(\text{BH}_3)_2(\text{BeH}_2)_4(\text{CH}_3\text{BeH})[(\text{CH}_3)_2\text{Be}]_4$	324	Honey
$[(\text{CH}_3)_2\text{BH}]_2(\text{BeH}_2)_4[(\text{CH}_3)_2\text{Be}]_2$	315	Glycerine
$(\text{BH}_3)_2(\text{BeH}_2)[(\text{CH}_3)_2\text{Be}]_2$	316	Water

(C) Improvements in the liquid properties of the BTEH liquids could conceivably result from the substitution of ethyl for methyl groups. From the viewpoint of energetic materials, however, this modification would be beneficial only if one ethyl group can be used in place of two or more methyl groups. The reaction of B<sub>4</sub>H<sub>10</sub> with Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> served to illustrate the feasibility of this approach. This and other reactions of Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> are summarized in Table 7.

(C) Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>/B<sub>4</sub>H<sub>10</sub> Reaction. The reaction of B<sub>4</sub>H<sub>10</sub> and Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> occurred readily at ambient temperature to yield the compound B<sub>3</sub>H<sub>7</sub>(C<sub>2</sub>H<sub>5</sub>BeH)(BeH<sub>2</sub>)BH<sub>3</sub> (specific impulse, 326 seconds). Comparison of the most likely molecular compositions of the two compounds B<sub>3</sub>H<sub>7</sub>(CH<sub>3</sub>BeH)<sub>2</sub>BH<sub>3</sub> and B<sub>3</sub>H<sub>7</sub>(C<sub>2</sub>H<sub>5</sub>BeH)(BeH<sub>2</sub>)BH<sub>3</sub>, for which the degree of polymerization is identical, demonstrates that one ethyl bridge group can be substituted for the two methyl bridge groups in the former compound. Furthermore, an improvement in the theoretical performance is obtained by altering the alkyl group (Table 2). Although both of the above compounds were quite mobile at ambient temperature, the C<sub>2</sub>H<sub>5</sub>-substituted material was still a mobile liquid at -40 C at which temperature the CH<sub>3</sub>-substituted material was a glass.

(C) Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>/B<sub>2</sub>H<sub>6</sub> Reaction. While the preparation of B<sub>3</sub>H<sub>7</sub>(C<sub>2</sub>H<sub>5</sub>BeH)BeH<sub>2</sub>BH<sub>3</sub> demonstrated that ethyl-substituted BTEH liquids could be prepared, and that one ethyl group could be substituted for two methyl groups with

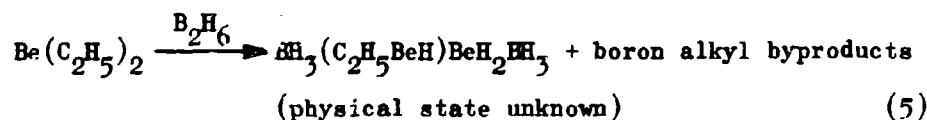
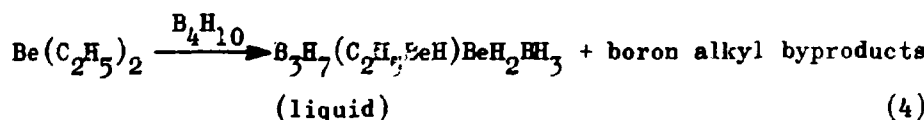
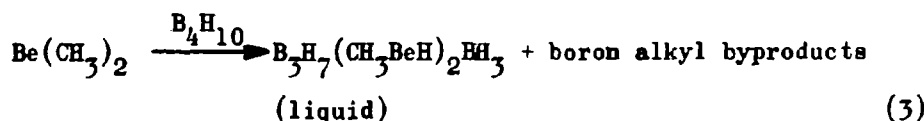
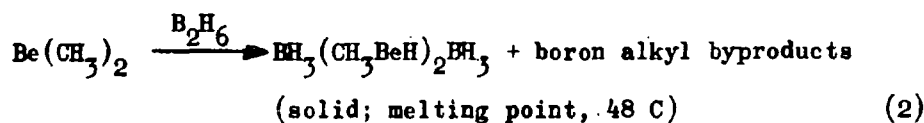
TABLE 7

SUMMARY OF  $\text{Be}(\text{C}_2\text{H}_5)_2$  REACTIONS  
(Conducted at Ambient Temperature)

Reactants	Mole Ratio	Comments
$\text{B}_4\text{H}_{10}/\text{Be}(\text{C}_2\text{H}_5)_2$	0.55	After a reaction time of 24 hours, a liquid was extracted from the reaction mixture. This material analyzed as $\text{B}_3\text{H}_7(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_3$ .
$\text{B}_2\text{H}_6/\text{Be}(\text{C}_2\text{H}_5)_2$	0.8 and 0.4	Rapid hydriding of the metal alkyl occurred. Both $\text{Be}(\text{BH}_4)_2$ and impure $\text{BeH}_2$ were formed during these experiments.
$\text{Be}(\text{BH}_4)_2/\text{Be}(\text{C}_2\text{H}_5)_2$	0.8	A volatile liquid was formed which analyzed as $\text{C}_2\text{H}_5\text{BH}_2(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_3$ . The material decomposed at ambient temperature to yield $\text{B}(\text{C}_2\text{H}_5)_3$ and nonvolatile solids.
$[(\text{C}_2\text{H}_5)_2\text{BH}]_2/\text{Be}(\text{C}_2\text{H}_5)_2$	2.0	All attempts to prepare $\text{BeH}_2[\text{HB}(\text{C}_2\text{H}_5)_2]_2$ by this reaction were unsuccessful. The reaction product decomposed to yield $\text{B}(\text{C}_2\text{H}_5)_3$ and nonvolatile solids corresponding to $(\text{BeH}_2)_x[\text{B}(\text{C}_2\text{H}_5)_3]_{2-x}$ .

some improvement in theoretical performance, it did not show unequivocally the effect of ethyl groups on the fluidity of BTBH liquids. Both the methyl and ethyl compounds in question were triborane terminated, and triborane termination itself results in good fluidity.

- (C) Because the reactions of tetraborane appear to parallel those of diborane (compare Eq. 2 and 3), the synthesis of  $\text{BH}_3(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_3$  from  $\text{B}_2\text{H}_6$  and  $\text{Be}(\text{C}_2\text{H}_5)_2$  was attempted (Eq. 5). Comparison of the physical state of this compound with that of  $\text{BH}_3(\text{CH}_3\text{BeH})_2\text{BH}_3$  would demonstrate more clearly the effect of ethyl groups on the physical state of BTBH liquids.



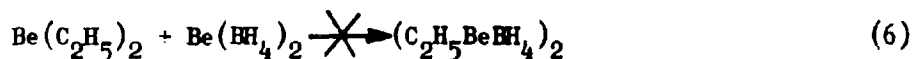
- (C) The  $\text{Be}(\text{C}_2\text{H}_5)_2/\text{B}_2\text{H}_6$  reaction, when conducted at mole ratios of 1.25 and 2.18, failed to yield any liquid beryllium products. Instead, the reactions proceeded rapidly to form solid boron alkyl-terminated beryllium hydride and  $\text{Be}(\text{BH}_4)_2$ .

- (C)  $\text{Be}(\text{BH}_4)_2/\text{Be}(\text{C}_2\text{H}_5)_2$  Reaction. The subsequent approach to the synthesis of a  $\text{BH}_3$ -terminated, ethyl-substituted liquid was the attempted preparation of  $\text{BH}_3(\text{C}_2\text{H}_5\text{BeH})_2\text{BH}_3$  or  $(\text{C}_2\text{H}_5\text{BeBH}_4)_2$ . The preparation of this compound was attempted via a method analogous to that used for the synthesis of  $(\text{CH}_3\text{BeBH}_4)_2$ , i.e., the reaction of the beryllium alkyl with  $\text{Be}(\text{BH}_4)_2$  (l.f. 8).



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- (C) Rapid solution of  $\text{Be}(\text{BH}_4)_2$  by  $\text{Be}(\text{C}_2\text{H}_5)_2$  occurred at ambient temperature, but the reaction product was not the expected  $(\text{C}_2\text{H}_5\text{BeBH}_4)_2$  (Eq. 6).



Instead of  $(\text{C}_2\text{H}_5\text{BeBH}_4)_2$ , a volatile liquid compound,  $\text{BH}_3(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_2\text{C}_2\text{H}_5$  (specific impulse, 311 seconds), was obtained. Based on this reaction and those run between  $\text{Be}(\text{C}_2\text{H}_5)_2$  and other B-H containing materials, it was evident that under comparable conditions, the  $\text{Be}-\text{C}_2\text{H}_5$  bond undergoes hydriding more easily than the  $\text{Be}-\text{CH}_3$  bond.

- (C) Partial characterization was made of  $\text{BH}_3(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_2\text{C}_2\text{H}_5$ . The material exhibited a vapor pressure of 2 mm Hg at 25 C and had a melting point  $< -40$  C. The compound decomposed at ambient temperature, however, to yield  $\text{B}(\text{C}_2\text{H}_5)_3$ , and nonvolatile solids.

- (C) Reaction of  $\text{Be}(\text{C}_2\text{H}_5)_2$  and Tetraethyldiborane. Based upon the reaction of  $\text{Be}(\text{C}_2\text{H}_5)_2$  and  $\text{B}_2\text{H}_6$  (described previously), it might be expected that alkyl-diboranes would also result in the formation of "impure  $\text{BeH}_2$ ". However, the reaction between  $\text{Be}(\text{C}_2\text{H}_5)_2$  and tetraethyldiborane,  $[\text{BH}(\text{C}_2\text{H}_5)_2]_2$ , has been reported to yield a stable, liquid complex,  $\text{BeH}_2[\text{BH}(\text{C}_2\text{H}_5)_2]_2$  (Ref. 9). Because there was a desire to use  $\text{BeH}_2[\text{BH}(\text{C}_2\text{H}_5)_2]_2$  as an intermediate in the formation of BTBH liquids, some effort was directed toward its preparation and isolation.

- (C) The previous work conducted at Rocketdyne under Contract AF04(611)-8550 on the  $\text{Be}(\text{C}_2\text{H}_5)_2/[\text{BH}(\text{C}_2\text{H}_5)_2]_2$  system indicated that the initial product formed dissociated to give a volatile compound containing hydrolyzable ethyl groups (Ref. 1). These results suggested the volatilization of  $\text{Be}-\text{C}_2\text{H}_5$  groups in the form of a complex because of incomplete hydriding of the  $\text{Be}-\text{C}_2\text{H}_5$  bonds. Consequently, an experiment was conducted to establish the degree of hydriding of the  $\text{Be}(\text{C}_2\text{H}_5)_2$  by the diborane derivative.

- (C) A 2:1 mixture of  $[(\text{C}_2\text{H}_5)_2\text{BH}]_2$  and  $\text{Be}(\text{C}_2\text{H}_5)_2$  was prepared in the high-vacuum system and was permitted to warm from  $-196$  C to ambient temperature. While

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warming the mixture to ambient temperature, the following transformations were observed: (1) melting of the components to a clear mobile solution; (2) rapid formation of a precipitate, just below 0 C, sufficiently thick to stop stirring; and (3) rapid dissolution of the solid to yield a clear mobile liquid. Subsequent hydrolysis of this reaction mixture yielded hydrogen containing only 0.1 mole percent ethane. The virtual absence of ethane in the gas formed after hydrolysis indicated a near-quantitative transfer of ethyl groups from beryllium to boron as shown in Eq. 7.



- (C) A duplicate of the preceding experiment was run and efforts were made to isolate the complex shown in Eq. 6. Separation of the byproduct  $\text{B}(\text{C}_2\text{H}_5)_3$ , was attempted by maintaining the reactor at 0 C while removing the volatile materials by vacuum condensation. The residual material was a clear glass, while the volatiles consisted of a mixture of solid and liquid at -78 C, which converted to a clear liquid at ambient temperature. Analyses of the volatile fraction demonstrated the presence of beryllium, hydrolyzable ethyl groups, hydridic hydrogen and boron; approximately one-half of the beryllium initially present as  $\text{Be}(\text{C}_2\text{H}_5)_2$  was found in the volatile fraction. The nonvolatile glass had a Be:B ratio of 3.4:1, and the gas formed after hydrolysis was hydrogen containing only trace amounts of ethane.
- (C) Despite the fact that it was demonstrated that hydriding of the  $\text{Be}(\text{C}_2\text{H}_5)_2$  by  $[\text{BH}(\text{C}_2\text{H}_5)_2]_2$  occurred in the stoichiometry shown in Eq. 6, the isolation of the reported nonvolatile  $\text{BeH}_2[\text{BH}(\text{C}_2\text{H}_5)_2]_2$  was not possible. Because incomplete hydriding of the beryllium does not appear to be the reason for the failure to isolate the complex, it was concluded that the stability of the complex is marginal. The dissociation of the liquid product to nonvolatile species, most likely boron alkyl-terminated beryllium hydride, and volatile products other than  $\text{B}(\text{C}_2\text{H}_5)_3$  prevented isolation and identification of the initially formed beryllium material. These results are consistent with the more recent studies conducted at Ethyl Corporation on the stability of  $\text{BeH}_2[\text{BH}(\text{C}_2\text{H}_5)_2]_2$ /Beane binary systems (Ref. 10).

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## Reaction of $B_4H_{10}$ and Alkylberyllium Hydrides

- (C) In the absence of solvents, the reaction of  $B_4H_{10}$  with  $Be(CH_3)_2$  or  $Be(C_2H_5)_2$  can be explained best by a reaction mechanism involving depolymerization and hydriding of the beryllium dialkyl, and subsequent complexing of the Be-H species by the cleavage products of  $B_4H_{10}$  ( $BH_3$  and  $B_3H_7$ ). Because such BTBH liquids as  $B_3H_7(C_2H_5BeH)BeH_2BH_3$  (specific impulse, 326 seconds),  $B_3H_7(CH_3BeH)_2BeH_2BH_3$  (specific impulse, 326 seconds) and other high-energy materials were formed from the reaction of  $B_4H_{10}$  and the beryllium dialkyls, it was believed that a better fuel might be produced from the action of  $B_4H_{10}$  on the alkyl beryllium hydride or dialkylberyllium-alkylberyllium hydride copolymers. A summary of the reactions investigated is presented in Table 8.
- (C)  $B_4H_{10}/[(C_2H_5)_2Be \cdot C_2H_5BeH]$  Reaction. The ambient temperature decomposition of  $Be(C_2H_5)_2$  (described subsequently) results in the formation of the copolymer  $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ . The reaction of this material with  $B_4H_{10}$  and with  $B_2H_6/B_4H_{10}$  mixtures as a preparative method for ethyl-substituted BTBH liquids was investigated.
- (C) The reaction of pure  $B_4H_{10}$  with the copolymer at ambient temperature was conducted at a  $Be/B_4H_{10}$  ratio of 2.6. Under these conditions, the solid yielded a liquid after 4 days. The only volatile product observed was  $B(C_2H_5)_3$ . The average composition of the mobile, nonvolatile liquid product was  $B_3H_7(C_2H_5BeH)_4BeH_2B_3H_7$  (specific impulse, 315 seconds).
- (C)  $B_4H_{10}/B_2H_6/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$  Reaction. To increase the rate of reaction of  $B_4H_{10}$  with the copolymer and possibly the hydride content of the liquid product as well, a reaction was carried out between the copolymer and a mixture of  $B_4H_{10}$  and  $B_2H_6$ . At a  $B_4H_{10}/B_2H_6/Be$  ratio of 3.7:1.0:8.4, the time required to convert the copolymer to a liquid product was reduced to 2 days. Although the  $B_2H_6$  served to promote the reaction of the copolymer with  $B_4H_{10}$ , it also caused the formation of a less polymeric liquid product:  $B_3H_7(C_2H_5BeH)_3BeH_2B_3H_7$  (specific impulse, 317 seconds).

TABLE 8

SUMMARY OF  $B_4H_{10}$ /ALKYLBERYLLIUM HYDRIDE REACTIONS  
(Conducted at Ambient Temperature)

Reactants	Mole Ratio	Comments
$B_4H_{10}/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$	0.6*	An ethyl-substituted BTHH liquid, $(B_3H_7)_2(C_2H_5BeH)_4BeH_2$ , was isolated from the reaction mixture.
$B_4H_{10}/B_2H_6/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$	3.7/1.0/8.4*	The addition of $B_2H_6$ caused an increased reaction rate and resulted in the formation of a BTHH liquid with a lower degree of polymerization. Analyses of the liquid corresponded to $(B_3H_7)_2(C_2H_5BeH)_3BeH_2$ .
$B_4H_{10}/(C_2H_5BeH)_x$	0.4*	The reaction proceeded rapidly in toluene to yield insoluble solids, but no liquids.
$B_4H_{10}/B_2H_6/(CH_3BeH)_x$	2.3/1.0/5.0*	Conversion of the solid $(CH_3BeH)_x$ to a liquid occurred in 3 hours. The analyses of the reaction product indicated it to be a 48:52 mixture of $B_3H_7(CH_3BeH)_5[Be(CH_3)_2]_2B_3H_7$ and $B_3H_7(CH_3BeH)_6[Be(CH_3)_2]_2H(CH_3)_2$ .

\*The calculated values for the polymeric beryllium compounds were based on the monomer.

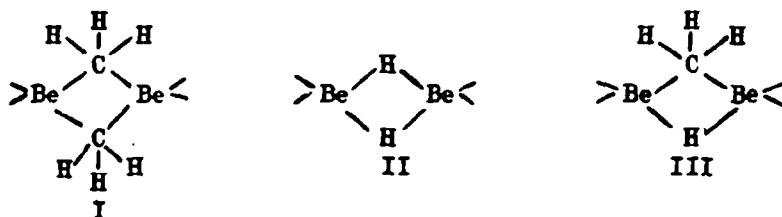
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- (C)  $B_4H_{10}/C_2H_5BeH$  Reaction. The effect of a solvent on the reaction of  $B_4H_{10}$  and alkylberyllium hydrides was investigated. For this purpose,  $(C_2H_5BeH)_x$  was chosen because of its solubility in toluene. The results of the reaction illustrated the competitive reactions which can occur in systems of the type studied during the course of this contract.
- (C) The reaction of  $B_4H_{10}$  and  $(C_2H_5BeH)_x$  in toluene yielded only solids, rich in Be-H species, despite the use of a small  $B_4H_{10}/(C_2H_5BeH)_x$  mole ratio. The failure to obtain liquid products from this reaction is attributed to the hydriding of  $(C_2H_5BeH)_x$  to  $(BeH_2)_x$ , and the insolubility of the  $(BeH_2)_x$  in toluene. As a result, the formation and precipitation of  $(BeH_2)_x$  was a more favored reaction than that involving complexing of the  $(C_2H_5BeH)_x$  or  $(BeH_2)_x$  by  $B_4H_{10}$ . These results are the same as those obtained from the reaction of liquid  $B_4H_{10}$  and  $Be(CH_3)_2$ .
- (C)  $B_4H_{10}/B_2H_6/(CH_3BeH)_x$  Reaction. A  $B_4H_{10}/B_2H_6$  mixture converted  $(CH_3BeH)_x$  to a liquid in 3 hours when a  $B_4H_{10}/CH_3BeH/B_2H_6$  of 2.34/5.00/1.00 was used. During this reaction time, however, little hydriding of the  $CH_3BeH$  occurred; only trace amounts of  $B(CH_3)_3$  were obtained. The principal volatile product was  $(CH_3BeBH_4)_2$ , suggesting that the  $B_2H_6$  caused some unzipping of the  $(CH_3BeH)_x$  polymer.
- (C) Analyses of the nonvolatile liquid product were best explained by assuming a 48:52 mixture of  $B_3H_7(CH_3BeH)_5[Be(CH_3)_2]B_3H_7$  and  $B_3H_7(CH_3BeH)_6[Be(CH_3)_2]BH(CH_3)_2$ . Because end-group analyses for boron of the  $(CH_3BeH)_x$ , prepared from  $(BeH_2)_x$   $[B(C_2H_5)_3]_2$  and  $Be(CH_3)_2$ , had indicated a degree of polymerization of 26, there was little doubt that its reaction with the  $B_4H_{10}/B_2H_6$  mixture had caused chain-shortening. The failure to obtain a more hydrided BTEH liquid than observed was thought to be the consequence of the short reaction time used. To test this postulate, a sample of the  $B_2H_6/B_4H_{10}/(CH_3BeH)_x$  reaction products was treated with an additional quantity of  $B_2H_6$  and  $B_4H_{10}$  for 2.5 hours. The resulting compound analyzed as  $B_3H_7(CH_3BeH)_6BH_2CH_3$ .

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## Problems of Hydriding BTHH Liquids

- (C) The reaction of  $B_4H_{10}$  or  $B_2H_6/B_4H_{10}$  mixtures with alkylberyllium hydrides failed to yield BTHH liquids of significantly greater hydridic hydrogen contents than those obtained from similar reactions with dialkylberyllium compounds. These observations may be a consequence of a combination of several factors.
- (C) X-ray data indicate that the angles in the four-membered rings of the  $Be(CH_3)_2$  chains are Be-C-Be, 66 degrees and C-Be-C, 114 degrees. Although no structural data exist for  $(BeH_2)_x$ , it is presumed that the Be-H-Be angle should be greater than 66 degrees and the H-Be-H angle should be less than 114 degrees because of the better orbital overlap of the spherical s orbital of H with the two beryllium  $sp^3$  orbitals when compared with the overlap of the narrower  $sp^3$  orbital of carbon.
- (C) On this basis, an explanation for the facile replacement of approximately one-half of the methyl groups in  $Be(CH_3)_2$  (I) by hydrogen may be invoked.

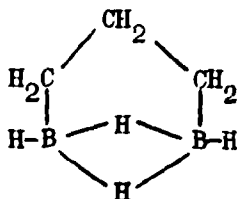


When one of the two bridging  $CH_3$  groups of  $Be(CH_3)_2$  is replaced by H, to give structure III, the tendency is for the Be atoms to move closer together, reducing the Be-C-Be angle to less than 66 degrees. The resulting increased overlap of the three  $sp^3$  orbitals makes a stronger methyl bridge bond, and as a result, one more difficult to replace in structure III than in structure I. Consequently, even though the formation of  $BeH_2$ (II) units should be favored thermodynamically, replacement of the remaining  $CH_3$  by H becomes kinetically controlled. Potential solutions to this problem are outlined in the Summary and Recommendations section of this report.

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## Reactions of Metathetical $(\text{BeH}_2)_x$

- (C) Several attempts were made to prepare BTH liquids from the reaction of metathetical  $(\text{BeH}_2)_x$ , synthesized from the reaction of  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{Be}(\text{BH}_4)_2$  (Ref. 11), and boron-hydrogen containing compounds. While reactions were observed in the systems investigated, none led to the isolation of a liquid beryllium compound.
- (C)  $\text{B}_4\text{H}_{10}/(\text{BeH}_2)_x$  Reaction. The work performed on the reactions of boron hydrides and beryllium alkyls demonstrated that the preparation of liquid beryllium compounds with specific impulses  $>310$  seconds is easily achievable (Ref. 1). However, a different approach to the formation of BTH liquids of higher specific impulse values might result from the reaction of  $\text{B}_4\text{H}_{10}$ , for example, with  $(\text{BeH}_2)_x$ .
- (C) The reaction of  $\text{B}_4\text{H}_{10}$  and  $(\text{BeH}_2)_x$  at ambient temperature during 4 days resulted in the formation of  $\text{H}_2$  and  $\text{Be}(\text{BH}_4)_2$ , but no liquids. The yield of  $\text{Be}(\text{BH}_4)_2$  was 20 percent (based on the beryllium hydride used), with only a 25 percent recovery of the  $\text{B}_4\text{H}_{10}$  used. The formation of  $\text{Be}(\text{BH}_4)_2$  from  $\text{B}_4\text{H}_{10}$  and  $(\text{BeH}_2)_x$  at ambient temperature was undoubtedly caused by the formation of  $\text{BH}_3$  groups via the decomposition of  $\text{B}_4\text{H}_{10}$ .
- (C) 1,2-Trimethylenediborane/ $\text{BeH}_2$  Reaction. The reaction of 1,2-trimethylenediborane (Ref. 12)



and metathetical  $(\text{BeH}_2)_x$  was also investigated as a method for forming BTH liquids. Although the reactions of  $\text{Be}(\text{BH}_4)_2$  (Ref. 8),  $\text{B}_2\text{H}_6$  (Ref. 8), and  $\text{B}_4\text{H}_{10}$  with metathetical  $(\text{BeH}_2)_x$  yielded only sublimable solid products, the presence of methylene groups in the 1,2-trimethylenediborane could serve to alter the physical state of the products.

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- (C) A mixture of the diborane derivative (containing some n-propyldiborane, a byproduct of the preparation of 1,2-trimethylenediborane) and metathetical  $(\text{BeH}_2)_x$  formed a thick paste at ambient temperature which exhibited no apparent change after 16 hours. Heating the mixture at 57 C for 4 hours resulted in the formation of a volatile solid,  $\text{Be}(\text{BH}_4)_2$ . No further investigation of this system was made because the main portion of the reaction mixture remained a pasty solid.

## ALANE-TERMINATED BERYLLIUM LIQUIDS

- (C) As a result of experiments conducted at Rocketdyne under Contract AF04(611)-9882, it was determined that Beane reacted with  $\text{Al}(\text{CH}_3)_3$  at elevated temperatures, and that concentration of the reaction products afforded a liquid product containing both beryllium and aluminum (Ref. 13). Although performance calculations indicate that the BTRH liquids are potentially higher-performing neat fuels than the alane-terminated beryllium hydrides (ATRH) liquids, the latter materials have other applications including:

1. Use as liquid carriers for Beane in heterogeneous propellants
2. Precursors for BTRH liquids

Since initiation of work on the present contract, gelled systems of ATRH and Beane have been prepared (Ref. 2). Further exploitation of the use of ATRH liquids in heterogeneous systems is being investigated under Contract F04611-67-C-0038 (Ref. 14). The following discussion is, therefore, confined to investigations concerning the preparation of ATRH liquids and their interaction with boron-containing compounds.

### Reaction of Beane With $\text{Al}(\text{CH}_3)_3$

- (C) The reaction of Beane with  $\text{Al}(\text{CH}_3)_3$  was observed to be time and temperature dependent; at temperatures below 120 C the rate of reaction was quite slow. A determination was made of the rate of reaction between Beane and  $\text{Al}(\text{CH}_3)_3$



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at 130 C by conducting a series of experiments in which 2:1 mixtures of  $\text{Al}(\text{CH}_3)_3$  and Beane (96 percent purity) were used. The rate of disappearance of solid Beane (Fig. 1) fitted a simple second-order expression (as determined by the method presented in Ref. 15), although the significance of this is not known. As shown by the plot in Fig. 1, the disappearance of the Beane was near-quantitative (98.6 percent) after 48 hours.

- (C) The preliminary experiments resulted in no evidence for the formation of noncondensable gases during the reaction of Beane with  $\text{Al}(\text{CH}_3)_3$  [Contract AF04(611)-9882]. The liquid product isolated, however, had an analytically established H:Be ratio less than 2, suggesting that reaction of the Beane was accompanied by hydrogen-methyl group exchange. The low H:Be ratio would then arise from the removal of Al-H species during the isolation of the main product.
- (C) An experiment was performed to determine if any Al-H species could be identified among the volatile products from the  $\text{Al}(\text{CH}_3)_3$ /Beane reaction. After heating a 1.7:1 mixture of  $\text{Al}(\text{CH}_3)_3$  and Beane at 120 C for 24 hours, the volatile materials were removed by vacuum distillation. Analyses of the volatile products revealed the presence of a hydrogen-containing aluminum species, most likely  $[(\text{CH}_3)_2\text{AlH}]_3$ , along with unreacted  $\text{Al}(\text{CH}_3)_3$ . The results of this experiment strongly suggest that the reaction of  $\text{Al}(\text{CH}_3)_3$  and Beane occurs as a consequence of hydrogen-methyl group exchange.
- (C) Composition vs Reaction Time. The series of experiments used for establishing the rate of reaction of Beane with  $\text{Al}(\text{CH}_3)_3$  also served to indicate the variation of composition of the ATBH liquids with reaction time. While there was some scatter in the analytical data obtained with the ATBH materials, i.e., after removal of the excess  $\text{Al}(\text{CH}_3)_3$  and any volatile reaction products, a trend toward decreased methyl group content in the ATBH material with reaction time was apparent. However, the best product still contained too much carbon for its use as a neat liquid fuel.

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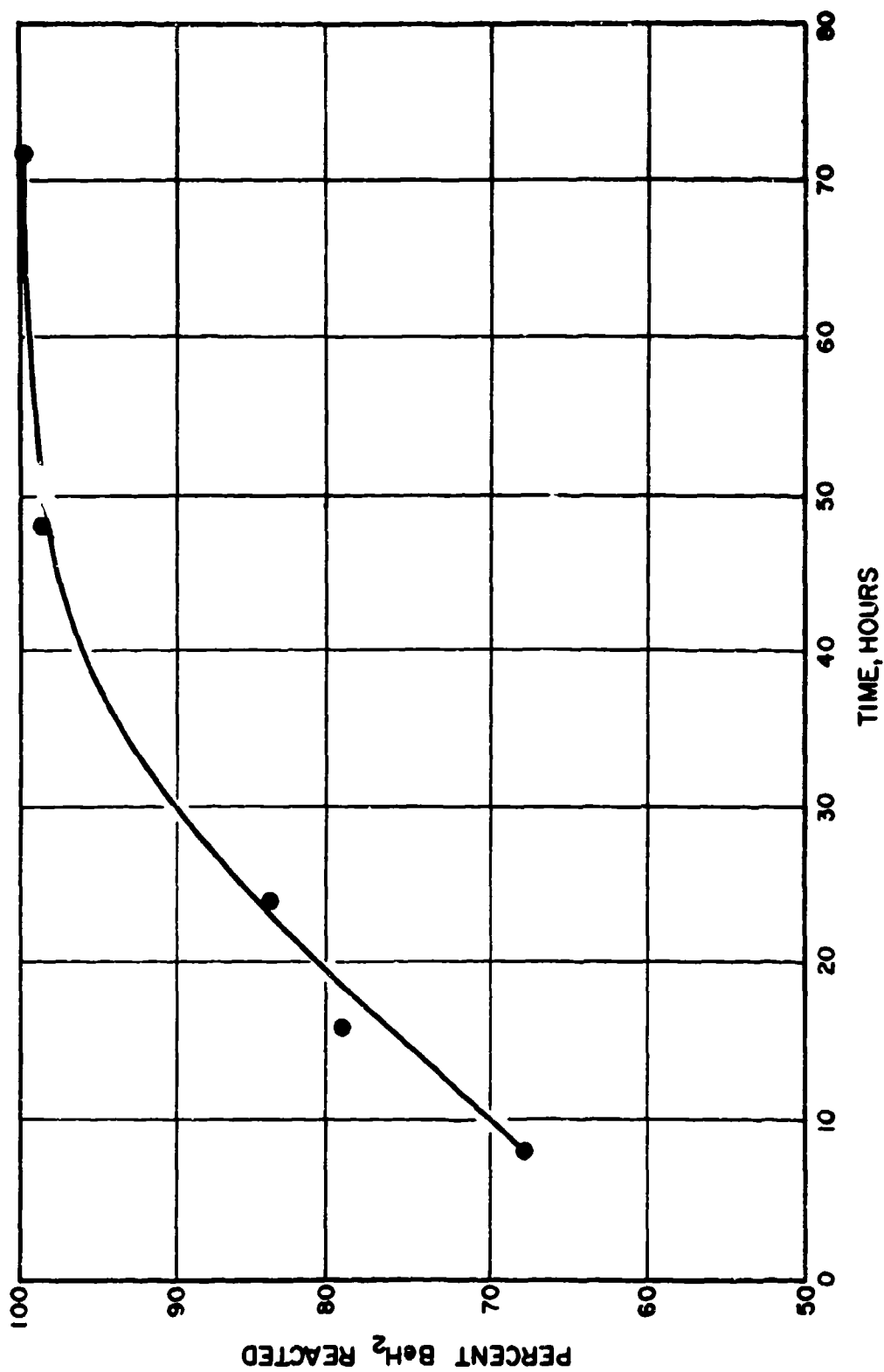


Figure 1. Rate of BeH<sub>2</sub> Reaction With Al(CH<sub>3</sub>)<sub>3</sub> at 130 C

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- (C) Nature of Insoluble Materials. As stated previously, the rate of reaction between Beane and  $\text{Al}(\text{CH}_3)_3$  is temperature dependent; for example, appreciable amounts of unreacted solids remained after short reaction times even at 130 C (Fig. 1). The nature of the unreacted solids remaining after reaction of  $\text{Al}(\text{CH}_3)_3$  and Beane (2.3:1 mole ratio) at 120 C for 16 hours was investigated. Isolation and analyses of the insoluble material revealed it to be unreacted Beane of a purity similar to that used (92 vs 96.6 weight percent). These data suggest that the formation of long-chain, insoluble species of the type  $(\text{BeH}_2)_x[\text{Al}(\text{CH}_3)_3]_2$  is not a part of the reaction sequence. Reaction via monomeric units or short chains of Beane may accordingly be important in the reaction mechanism.

## Reaction of Beane and Dimethylalane

- (C) Dimethylalane,  $[(\text{CH}_3)_2\text{AlH}]_3$ , reacts more slowly with Beane than does trimethylalane. A direct comparison of the reactivities of the two alanes was made using 2:1 alane-to-Beane mixtures. After 24 hours at 130 C, the amount of reaction was four times greater with  $\text{Al}(\text{CH}_3)_3$  than with the  $[(\text{CH}_3)_2\text{AlH}]_3$  (21 vs 84 weight percent  $\text{BeH}_2$  reacted.) The recovered ATBH liquid was quite viscous and complete removal of the excess dimethylalane from the product was not possible.
- (C) A reasonable explanation for the difference in behavior of the two alanes toward Beane is the chemical bonding involved. Assuming the Beane/alane reaction mechanism to involve monomeric species of the alane, the formation of such intermediates from  $[\text{Al}(\text{CH}_3)_2]_2$  should be easier than from  $[(\text{CH}_3)_2\text{AlH}]_3$  because Al-H-Al bridge bonds are stronger than Al-CH<sub>3</sub>-Al bridge bonds. On this basis, the greater reactivity of  $\text{Al}(\text{CH}_3)_3$  was not unexpected.

## Physical Properties of ATBH Liquids

- (C) The molecular structure of the ATBH liquids was assumed to be composed of chains of beryllium atoms appropriately connected by methyl and/or hydrogen

bridge bonds and terminated by aluminum alkyls. Evidence for this type of structure was based on the existence of known alkylalane complexes containing one unit of  $\text{BeH}_2$  (for example, Ref. 16), and the fact that infrared spectra of these materials are not composite spectrograms of  $(\text{CH}_3)_3\text{Al}$  or  $(\text{CH}_3)_2\text{AlH}$  and  $\text{BeH}_2$  or  $\text{CH}_3\text{BeH}$ .

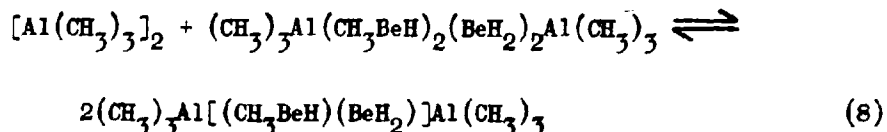
- (C) Measurements of some physical properties of selected ATBH liquids have been made (Ref. 2), and the data are presented in Table 9.

TABLE 9

SOME PHYSICAL PROPERTIES OF  $(\text{CH}_3)_3\text{Al}(\text{CH}_3\text{BeH})(\text{BeH}_2)_2\text{Al}(\text{CH}_3)_3$

Density (29 C), gm/cc	0.72
Thermal Stability (as gas evolution rate), cc/min/lb	$5.1 \times 10^{-2}$ (71 C or 160 F) $1.2 \times 10^{-4}$ (ambient temperature)
Specific Impulse (shifting equilibrium, 1000 - 14.7 psia, $\text{H}_2\text{O}_2$ ), seconds	297

It has been observed that the viscosity of the ATBH material can be varied simply by the addition or removal of  $\text{Al}(\text{CH}_3)_3$  from the complex. This indicates that the ATBH liquids can participate in an equilibrium of the type exemplified by Eq. 8, although simple dilution of the complex cannot be ignored.



Hydriding of ATBH Liquids

- (C) The quantitative reaction of  $\text{Al}(\text{CH}_3)_3$  and Beane in a 2:1 mole ratio and at a temperature of 130 C did not result in a liquid fuel with a specific impulse of  $\geq 330$  seconds. Therefore, attempts were made to improve the hydridic hydrogen contents of the ATBH liquids by reaction with boron

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hydrides and their derivatives. The net result of these reactions was not only partial replacement of the methyl groups by hydridic hydrogen, but also a near-quantitative displacement of the aluminum by boron.

- (C) The relative hydriding ability of  $B_2H_6$ ,  $B_4H_{10}$ , and  $Be(BH_4)_2$  on a single ATBH liquid was investigated. The improvement in the Be:H values was based upon the initial Be:H:CH<sub>3</sub> values determined for the ATBH liquid being used. A comparison of the results (Table 10) indicated that the reactivity of the three hydriding agents with the ATBH material decreased in the order  $B_4H_{10} > Be(BH_4)_2 > B_2H_6$ . In regard to the displacement of aluminum, the three reagents appeared to be equally effective, i.e., 80 to 85 percent of the aluminum was recovered as a methyl-substituted aluminum borohydride.

TABLE 10

## HYDRIDING OF ATBH LIQUID

Reagent	Quantity, millimoles	Be:H:CH <sub>3</sub> Ratio	
		ATBH Liquids	Product
$B_4H_{10}$	0.429	1.0:1.0:1.85	1.0:2.9:1.0
$Be(BH_4)_2$	0.452	1.0:1.0:1.85	1.0:1.8:0.92
$B_2H_6$	0.455	1.0:1.0:1.85	1.0:1.5:0.93

### Improved Preparations of Beryllium Alkyls

- (U) The  $Be(CH_3)_2$  and  $Be(C_2H_5)_2$  used in the preceding reactions were prepared by the Grignard procedure, and great care was taken in purifying these materials before use. Vacuum sublimation of  $Be(CH_3)_2$  from the magnesium salts formed during the preparative reaction often resulted in the cosublimation of an iodide-containing impurity (most likely  $CH_3BeI$ ). It was found that the iodide impurity could be converted to a nonvolatile substance by thermally soaking the crude product at 115 C. Subsequent sublimation of the  $Be(CH_3)_2$  then yielded material of 99+ percent purity.

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- (U) A convenient procedure for the preparation of ether-free  $\text{Be}(\text{C}_2\text{H}_5)_2$  was developed during the course of this contract. It was found that if the solid reaction products of  $\text{C}_2\text{H}_5\text{MgBr}$  and  $\text{BeCl}_2$  were extracted with benzene at ambient temperature, the  $\text{Be}(\text{C}_2\text{H}_5)_2$  which was recovered after a simple distillation was of 99+ percent purity. The benzene extraction was found to facilitate the recovery of the  $\text{Be}(\text{C}_2\text{H}_5)_2$  from the solid reaction products.

#### DECOMPOSITION OF $\text{Be}(\text{C}_2\text{H}_5)_2$ AT AMBIENT TEMPERATURE

- (U) Although  $\text{Be}(\text{C}_2\text{H}_5)_2$  undergoes pyrolysis at elevated temperatures (Ref. 17), no report of its instability at ambient temperature is cited in the literature. However, during the course of the present research effort, a slow decomposition of the metal alkyl was observed to occur at ambient temperature. The decomposition products of  $\text{Be}(\text{C}_2\text{H}_5)_2$  consisted of a beryllium-containing solid and unidentified gases. Analyses of the solid revealed it to be a copolymer of  $\text{Be}(\text{C}_2\text{H}_5)_2$  and  $\text{C}_2\text{H}_5\text{BeH}$ ,  $[(\text{C}_2\text{H}_5)_2\text{Be} \cdot \text{C}_2\text{H}_5\text{BeH}]_x$ .
- (C) It has been observed at Ethyl Corporation that the binary system  $\text{Be}(\text{C}_2\text{H}_5)_2/\text{Beane}$  slowly solidifies on standing at ambient temperature (Ref. 10). Furthermore, Beane coated with basic polymers such as Carbowax 1000, Epoxy resin, and polyesters when mixed with  $\text{Be}(\text{C}_2\text{H}_5)_2$  produced solids within a few days. The similarity between the behavior of neat  $\text{Be}(\text{C}_2\text{H}_5)_2$ , prepared by the Grignard method, which undoubtedly contained trace amounts of diethyl ether, and the Ethyl Corporation results suggests that the decomposition of  $\text{Be}(\text{C}_2\text{H}_5)_2$  is catalyzed by Lewis bases.

#### PYROLYSIS OF $\text{Be}(\text{C}_2\text{H}_5)_2$

- (C) The pyrolysis of  $\text{Be}(\text{C}_2\text{H}_5)_2$  has been reported to yield a liquid compound having the composition  $\text{C}(\text{BeH}_2\text{BeC}_2\text{H}_5)_4$  (Ref. 17). Because this compound represents a class of liquid fuels containing beryllium and hydrogen, but has no extraneous terminating groups, some effort was expended in attempting to prepare a pure sample of this material. Several

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samples of a nonvolatile liquid product were obtained from the pyrolysis of  $\text{Be}(\text{C}_2\text{H}_5)_2$  at 200 C. Although the ratios of the constituents of the pyrolysis product approached those expected for the composition  $\text{C}(\text{BeH}_2\text{BeC}_2\text{H}_5)_4$ , in no case was a pure sample obtained.

- (U) The failure to purify the liquid pyrolysis product by distillation appears to have been caused by the codistillation of a high-molecular-weight hydrocarbon formed during the pyrolysis. Mass spectral analyses of the ambient temperature volatile hydrocarbon byproducts disclosed not only ethane and ethylene (the principal products), but also hydrocarbons up through substituted pentanes. The formation of the hydrocarbons other than ethane and ethylene is attributed to the  $\text{Be}(\text{C}_2\text{H}_5)_2$  acting as a Ziegler-type polymerization catalyst for ethylene. The formation of still higher hydrocarbons of low volatility resulted in the formation of an intractable mixture containing the desired beryllium product.
- (U) Deuterolysis was used to demonstrate that the hydrocarbon was present as a physical contaminant rather than as a high-molecular-weight beryllium alkyl species. Deuterolysis of a distilled sample of the pyrolysis product did not yield any hydrocarbons heavier than methane and ethane containing C-D bonds as would be expected if they were chemically bound to the beryllium

**CONCLUSIONS AND SUMMARY**

- (C) This program has demonstrated that liquid beryllium hydrides may be prepared with theoretical specific impulses approaching 330 seconds (1000 ~ 14.7,  $H_2O_2$  oxidizer). It appears that higher borane fragments, such as  $B_3H_7$ , are better than simple  $BH_3$  groups as the terminating species for these liquids, inasmuch as liquids containing  $B_3H_7$  have good fluidity and other satisfactory properties coupled with high impulse. Further increases in  $BeH_2$  content are needed for the liquid beryllium hydrides to surpass the 330-second specific impulse level.
- (C) A summary of the important results supporting the above conclusions, as well as other aspects of this work, are as follows:
1. Reactions of  $B_4H_{10}$  with  $Be(CH_3)_2$  and  $Be(C_2H_5)_2$  resulted in the synthesis of compounds such as  $B_3H_7(CH_3BeH)_2BeH_2BH_3$  (329 seconds),  $B_3H_7(C_2H_5BeH)BeH_2BH_3$  (326 seconds),  $B_3H_7(CH_3BeH)_3BeH_2BH_3$  (326 seconds), and  $B_3H_7(CH_3BeH)_2BH_3$  (320 seconds).
  2. Previously it had been observed that the termination of BTEH liquids with two  $BH_3$  groups often yielded materials which underwent reversible dissociation. When one of the  $BH_3$  groups was replaced by a  $B_3H_7$  terminator, the tendency of the liquids to dissociate reversibly was eliminated.
  3. The preparation of  $B_3H_7(C_2H_5BeH)BeH_2BH_3$  demonstrated that it is possible to prepare ethyl-substituted BTEH analogs of previously known methyl-substituted liquids, and that one ethyl group replacing two methyl groups in such compounds leads to higher specific impulse.
  4. The preparation of liquids containing both ethyl and  $B_3H_7$  groups demonstrated that such compounds have good viscosities and low melting points.



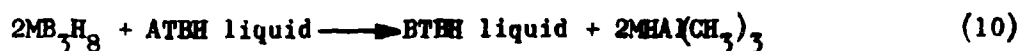
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5. The conversion rate of solid beryllium compounds to liquids by  $B_4H_{10}$  was greatly increased by the use of  $B_2H_6/B_4H_{10}$  mixtures. Possibly, the  $B_2H_6$  served as a depolymerization agent for  $Be(CH_3)_2$  and in so doing rendered the metal alkyl more reactive toward  $B_4H_{10}$ .
6. Neat  $B_4H_{10}$  reacted slowly with  $Be(CH_3)_2$ . Because of the instability of  $B_4H_{10}$  and the slowness of its reaction with  $Be(CH_3)_2$ , products in addition to the triborane-terminated materials were formed. The disproportionation of  $B_4H_{10}$ , however, was suppressed when  $B_2H_6/B_4H_{10}$  mixtures, rather than pure  $B_4H_{10}$ , were used.
7. The very reactive hydriding agents  $B_2H_6$  and  $Be(BH_4)_2$  reacted with  $Be(C_2H_5)_2$  and resulted in extensive hydriding of the beryllium. Under comparable experimental conditions, the extent of hydriding  $Be(CH_3)_2$  was much less.
8. The preparation of ATBH liquids from Beane and methylated alanes was investigated. Experimental conditions were established for the quantitative reaction of  $Al(CH_3)_3$  and Beane.
9. The reaction of ATBH liquids with  $B_2H_6$ ,  $B_4H_{10}$ , and  $Be(BH_4)_2$  proved the feasibility of using the ATBH liquids as precursors for BTBH materials. In each of the preceding reactions, the displacement of aluminum from the ATBH liquids by the B-H containing reagents was greater than 80 percent.
10. It was discovered that extremely pure  $Be(C_2H_5)_2$  undergoes decomposition at ambient temperature. The beryllium-containing decomposition product was found to have the composition  $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ , and was subsequently converted to liquids when reacted with  $B_4H_{10}$  and/or  $B_4H_{10}/B_2H_6$  mixtures.

**RECOMMENDATIONS**

- (C) The preparative route to the  $B_3H_7$ -terminated liquids has been the reactions of  $B_4H_{10}$  with various beryllium compounds. These reactions have proved to be very complex. On the other hand, reactions of the ternary system  $B_2H_6/B_4H_{10}/Be$  compound are less complex. It is recommended that additional work be performed on these ternary systems. This effort would include a determination of the optimum  $B_2H_6$  concentration, and its variation, if any, from one alkyl to another; and the optimum reaction time for maximum hydriding of the beryllium compound consistent with formation of serviceable liquid propellants.
- (C) The second important aspect of the tetraborane system should be based upon increasing the hydrogen content of the known triborane-terminated liquids. This may be approached in several ways. One method would be the treatment of the known liquids with metathetical  $BeH_2$ , a reaction which occurs readily with borane-terminated liquid compounds.
- (C) Another approach would be based on the observation that the formation of Be-H bonds from  $Be(C_2H_5)_2$  occurs much more readily than from  $Be(CH_3)_2$ . This difference in the reactivity of  $Be(CH_3)_2$  and  $Be(C_2H_5)_2$  may serve a useful purpose if instead of reacting  $B_4H_{10}$ , for example, with either pure  $Be(CH_3)_2$  or  $Be(C_2H_5)_2$ , a mixed alkyl,  $CH_3BeC_2H_5$ , or a copolymer of the two alkyls is used. The reaction of either one of these materials with a  $B_2H_6/B_4H_{10}$  mixture may result in a rapid and quantitative conversion of the Be- $C_2H_5$  bonds to Be-H bonds, leaving the Be- $CH_3$  bonds to serve as the groups that maintain liquid properties in the products.
- (C) Alternate methods to the preparation of triborane-terminated liquids should also be developed. The three reagents  $B_2H_6$ ,  $Be(BH_4)_2$ , and  $B_4H_{10}$  all react with concentrated ATBH materials and result in displacement of the alane terminators. Additional reactions, as shown by the following equations, may also be feasible.





The above reactions may not only prove to be more convenient than those involving  $\text{B}_4\text{H}_{10}$  and beryllium alkyls, but may also result in the formation of pure liquid beryllium compounds, free from side products introduced from the disproportionation of  $\text{B}_4\text{H}_{10}$ .

(C) Two additional approaches to the preparation of BTBH liquids are outlined below. These reactions are considered exploratory and would be given a lower priority than those presented above.

1. In the case of  $\text{B}_4\text{H}_{10}$ , it is believed that the bulkiness of the  $\text{B}_3\text{H}_7$  group helps prevent the triborane-terminated species from crystallizing. Similarly,  $\text{B}_5\text{H}_9$  and  $\text{B}_5\text{H}_{11}$  could yield bulky fragments,  $\text{B}_4\text{H}_6$  and  $\text{B}_4\text{H}_8$  respectively, which might serve as terminators and impart good physical properties to liquid beryllium fuels. The reactions of the pentaboranes with polymeric beryllium compounds should be explored.
2. The use of difunctional boranes such as 1,2-trimethylenediborane,  $\text{H}_2\text{BC}_3\text{H}_6\text{BH}_2$ , to link Be-Be segments and impart flexibility to the chain, did not yield BTBH liquids on reaction with metathetical  $\text{BeH}_2$ . However, more desirable reactions may result from the action of these materials on beryllium alkyls.

## EXPERIMENTAL DETAILS

### GENERAL

- (U) Handling and manipulation of pyrophoric and/or toxic materials were performed in high-vacuum systems or inert-gas, gloved boxes. Most reactions were conducted in round-bottom Pyrex reactors of varying volumes, fitted with Fischer-Porter needle valves. These reactors were connected to the high-vacuum systems by means of standard-tapered joints.

### Chemicals

- (U)  $\text{Be}(\text{BH}_4)_2$ . Beryllium borohydride was prepared by reacting  $\text{LiBH}_4$ - $\text{KBH}_4$  mixtures with  $\text{BeCl}_2$  (Ref. 11).
- (U) Beryllium Alkyls. Dimethylberyllium was prepared by the method of Gilman (Ref. 18). After thermal dissociation of the  $\text{Be}(\text{CH}_3)_2$ -etherate, iodide impurities were detected in the sublimed  $\text{Be}(\text{CH}_3)_2$ . Removal of this contaminant, possibly  $\text{CH}_3\text{BeI}$ , was accomplished by thermally soaking the crude  $\text{Be}(\text{CH}_3)_2$  at 115 C. Subsequent sublimation of the material treated in this manner yielded pure  $\text{Be}(\text{CH}_3)_2$ .
- (U) Ether-free  $\text{Be}(\text{C}_2\text{H}_5)_2$  was prepared by a modification of Goubeau's method (Ref. 17). Modification of Goubeau's procedure consisted of a benzene extraction of the solid mass formed from the Grignard reaction. Distillation of the benzene extract, after removal of the hydrocarbon, yielded  $\text{Be}(\text{C}_2\text{H}_5)_2$  (boiling point, 69 C at 0.11 mm Hg) in 55 percent yield and 99+ percent purity.
- (U)  $\text{B}_4\text{H}_{10}$ . Tetraborane was synthesized by the decomposition of  $\text{B}_2\text{H}_6$  under pressure essentially as described by Kodama (Ref. 19). As determined by infrared spectroscopy, the material was pure after fractional condensation.

- (U) Solvents. Solvents were obtained from various commercial sources, dried over  $\text{LiAlH}_4$ , and stored over  $\text{LiAlH}_4$  until used.

#### ANALYTICAL PROCEDURES

- (U) The gases evolved after acid hydrolysis were removed to a known volume of the high-vacuum system, by means of a Toepler or Sprengel pump, and measured. The gases were assayed, by mass spectrometric techniques, and the relative amounts of hydrogen and  $\text{CH}_4$  or  $\text{C}_2\text{H}_6$  were determined. The amount of hydrocarbon found was presumed to be a direct measurement of the bridging alkyl group content. The hydrolysate was then analyzed for Be and B or Al.
- (U) The most reliable analytical results for beryllium were obtained by atomic absorption spectrophotometry. Precipitation of the beryllium as the cupferronate yielded consistently low results. Boron was determined as described in Ref. 1. An alternate analysis (Ref. 20), a rapid flame spectrophotometric procedure, was utilized late in the program and was found to yield equally reliable results. Aluminum was determined gravimetrically by the use of 8-hydroxyquinoline.
- (U) In most instances, no direct measurement was made of the alkyl substituents bound to boron. Instead, the extent of boron substitution was determined by the difference between the sum of the weights of the directly measured constituents and the weight of the analytical sample. In the remaining instances, the following procedure was used to determine directly the amount of boron-alkyl substitution.

#### Direct B-Alkyl Group Analysis

- (C) The analysis of BTBH liquids for boron-bound alkyl groups was developed with mixtures of  $\text{Be}(\text{CH}_3)_2$  and  $\text{B}_2\text{H}_6$ . The procedure was as follows. Weighed samples of  $\text{Be}(\text{CH}_3)_2$  (0.0420 gram) and  $\text{B}_2\text{H}_6$  (0.0261 gram) were sealed into a bulb to which were attached, by magnetic break-seals, two reagent ampoules.

One ampoule contained a mixture of xylene (2.0 milliliters) and 12 N HCl (0.6 milliliter) and the second contained propionic anhydride (4.0 milliliters). The  $B_2H_6/Be(CH_3)_2$  mixture was reacted for 18.5 hours to ensure equilibration of the  $CH_3$  groups between beryllium and boron species in the liquid product.

- (U) The analysis was initiated by introducing the xylene/aqueous acid mixture onto the synthesized liquid complex. The gases formed at ambient temperature were collected, after passing through a  $-196^\circ C$  trap, and measured in an automatic Toepler system. All materials not passing  $-196^\circ C$  were returned to the bulb, and the bulb was resealed and heated at  $125^\circ C$  for 16 hours to ensure completion of the hydrolysis. Any additional gases formed were again collected.
- (U) All remaining volatiles were resealed in the bulb and the propionic anhydride was introduced at ambient temperature. Cleavage of the  $B-CH_3$  bonds by propionic acid was accomplished during 16 hours at  $140^\circ C$ . As previously, the gases produced were passed through a  $-196^\circ C$  trap, collected, and measured. Mass spectrometric analyses of the gaseous products were then performed. The accuracy of the analyses is demonstrated by the following data. Calculated were: Be, 1.07 matoms; B, 1.89 matoms; hydridic hydrogen, 5.66 mmoles; and total  $CH_3$  groups, 2.14 mmoles. Found were: Be, 1.02 matoms; B, 1.89 matoms; hydridic hydrogen, 5.60 mmoles; and total  $CH_3$  groups, 2.18 mmoles.

#### $B_4H_{10}/Be(CH_3)_2$ REACTIONS

##### Physical State of $B_4H_{10}$ and its Reactivity

- (C) The experiments conducted to determine how the physical state of  $B_4H_{10}$  altered its reaction with  $Be(CH_3)_2$  were performed in the following manner. To a heavy-wall cylindrical reactor containing  $Be(CH_3)_2$  (0.3535 gram, 9.05 mmoles) was added liquid  $B_4H_{10}$  (0.4794 gram, 8.00 mmoles). During

the second experiment,  $\text{Be}(\text{CH}_3)_2$  (0.3577 gram, 9.15 mmoles) was added to one arm of a heavy-wall inverted Y-reactor and liquid  $\text{B}_4\text{H}_{10}$  (0.4764 gram, 8.94 mmoles) condensed in the second arm of the reactor.

- (C) Total liquefaction of the  $\text{Be}(\text{CH}_3)_2$  in the vapor-phase reaction occurred in 26 hours. The liquid-phase reaction after this same time yielded primarily solids suspended in the unreacted  $\text{B}_4\text{H}_{10}$  and alkylboron products. The results of the reactions are presented in Table 11.

TABLE 11

REACTION OF  $\text{Be}(\text{CH}_3)_2$  WITH  $\text{B}_4\text{H}_{10}$  VAPOR AND WITH LIQUID  $\text{B}_4\text{H}_{10}$   
(Reaction Time 29.5 hours at Ambient Temperature)

Reactants, mmoles	Volatile Products,* mmoles					Nonvolatile Products, grams
	$\text{H}_2$	$(\text{CH}_3)_2\text{B}_2\text{H}_4$	$(\text{CH}_3)_4\text{B}_2\text{H}_2$	$\text{B}(\text{CH}_3)_3$	$\text{B}_4\text{H}_{10}$	
$\text{Be}(\text{CH}_3)_2$ , 9.15	2.50	1.13	0.17	1.94	3.35	Liquid, 0.3913
$\text{B}_4\text{H}_{10}$ (vapor), 8.94						Solid, 0.0586
$\text{Be}(\text{CH}_3)_2$ , 9.05	2.08	--	--	3.46	4.42	Solid, 0.0154
$\text{B}_4\text{H}_{10}$ (liquid), 8.99						Liquid, 0.040

\*In addition to the tabulated volatile products, trace amounts of  $(\text{CH}_3\text{BeBH}_4)_2$ ,  $\text{Be}(\text{BH}_4)_2$ , and an unstable material, believed to be a methyl-substituted beryllium borohydride, were obtained during both experiments.

- (C) Analysis of a sample (0.0268 gram) of the liquid obtained from the vapor-phase reaction yielded  $\text{H}_2$  (2.67 mmoles), B (0.0108 gram, 1.0 matom), Be (0.0058 gram, 0.64 matom), and  $\text{CH}_4$  (0.35 mmole). The observed Be:B:H:CH<sub>3</sub> ratios were 3.84:6.00:16.0:2.10; calculated for  $[(\text{CH}_3)_3\text{B}_3\text{H}_4]_2(\text{BeH}_2)_2(\text{CH}_3\text{BeH})_2$  were 4:6:16:2.

Variation of  $B_4H_{10}/Be(CH_3)_2$  Mole Ratio and Reaction Time

- (C) The data presented in Table 12 summarize the results obtained when the  $B_4H_{10}/Be(CH_3)_2$  mole ratio and the reaction time were varied. Analyses of the liquid products obtained from experiments No. 2, 4, and 5 were as follows.
- (C) Liquid Product, Experiment 2. Hydrolysis of a 0.0268 gram sample yielded  $H_2$  (2.67 mmoles), B (0.0108 gram, 1.0 matom), Be (0.0058 gram, 0.64 matom), and  $CH_4$  (0.35 mmole). The Be:B:H: $CH_3$  ratios were 3.84:6.00:16.0:2.10; calculated for  $[(CH_3)_3B_3H_4](BeH_2)_2(CH_3BeH)_2$  were: 4:6:16:2.
- (C) Liquid Product, Experiment 4. The liquid product was first extracted with n-hexane. The hexane filtrate was concentrated and the residual liquid material was analyzed. Hydrolysis of a 0.0357-gram sample yielded  $H_2$  (4.12 mmoles), B (0.0129 gram, 1.19 matoms), Be (0.0081 gram, 0.90 matom), and  $CH_4$  (0.50 mmole). The Be:B:H: $CH_3$  ratios derived from these results were: 3.02:4.00:13.8: ; calculated for  $B_3H_7(CH_3BeH)_2BeH_2BH_3$  were: 3:4:15:2.
- (C) Liquid Product, Experiment 5. The liquid product was processed in the same manner as for experiment No. 4. Subsequent hydrolysis of a 0.0418-gram sample yielded:  $H_2$  (4.07 mmoles), B (0.0153 gram, 1.41 matoms), Be (0.0063 gram, 0.70 matom), and  $CH_4$  (0.60 mmole). The Be:B:H: $CH_3$  ratios of 2.00:4.04:11.6:1.72 approached those calculated for  $B_3H_7(CH_3BeH)_2BH_2CH_3$ , i.e., 2:4:12:2.

$B_4H_{10}/B_2H_6/(CH_3)_2Be$  Reactions

- (C) A summary of the reaction products formed from the titled reaction is presented in Table 12. Of these products, only the liquid from experiment No. 2 was analyzed. The compositions of the remaining two liquids were



TABLE 12

VARIATION OF  $B_4H_{10}$  (VAPOR) /  $Be(CH_3)_2$  MOLE RATIO AND REACTION TIME

Experiment No.	Reactants, moles	Reaction Time, hours	Volatile Products, moles										Nonvolatile Products, grams
			$B_2H_6$	$U_2$	$B_4H_{10}$	$B_3H_{11}$	$B(CH_3)_3$	$CH_3B_2H_5$	$(CH_3)_2B_2H_4$	$(CH_3)_4B_2H_2$	$Be(CH_3)_2$		
1	$Be(CH_3)_2$ , 9.99 $B_4H_{10}$ , 13.0	95	—	4.42	trace	0.35	—	0.50	3.66	0.95	4.35	Solids, 0.3102	
2	$Be(CH_3)_2$ , 9.15 $B_4H_{10}$ , 8.94	29	—	2.50	3.35	—	1.94	—	1.15	0.17	trace	Solids, 0.0906 Liquid, 0.5915	
3	$Be(CH_3)_2$ , 9.90 $B_4H_{10}$ , 19.82	29	0.24	5.55	9.04	0.04	0.11	0.05	3.70	—	—	Solids, 6.3778	
4	$Be(CH_3)_2$ , 18.1 $B_4H_{10}$ , 9.2	120	—	2.35	0.95	—	5.17	—	—	—	—	—, 0.392 —, unweighed	
5	$Be(CH_3)_2$ , 18.0 $B_4H_{10}$ , 9.3	120	—	2.38	Volatile products neither measured nor identified							—	Solids, unweighed

TABLE 13  
SUMMARY OF  $B_4H_{10}/B_2H_6/Be(CH_3)_2$  REACTIONS

Experiment No.	Reactants, moles	Reaction Time, hours	Volatile Products, mmoles					Nonvolatile Products, grams
			$H_2$	$B_2H_6$	$B_4H_{10}$	$B(CH_3)_3$	$(CH_3BeBH_4)_2$	
1	$Be(CH_3)_2$ , 3.87	8	0.12	0.14	3.06	0.70	0.40	Liquid, 0.1191
	$B_4H_{10}$ , 3.72							
	$B_2H_6$ , 0.92							
2	$Be(CH_3)_2$ , 4.03	7.5	Neither measured nor identified					Liquid, 0.1222
	$B_4H_{10}$ , 4.27							
	$B_2H_6$ , 1.25							
3	$Be(CH_3)_2$ , 4.81	15.3	0.39	—	3.89	1.17	0.88	Liquid, 0.20
	$B_4H_{10}$ , 4.89							
	$B_2H_6$ , 1.25							

estimated by material balance. The formulas derived for these materials were  $B_3H_7(CH_3BeH)_2[(CH_3)_2Be]_3BH_3$  (experiment No. 1) and  $B_3H_7[Be(CH_3)_2]_2(CH_3BeH)_2BH_3$  (experiment No. 3).

- (C) Analysis of Liquid Product, Experiment 2. The liquid product was analyzed by use of the sequential HCl/propionic acid procedure. The amounts of each constituent found and those calculated for a 39:61 mixture of  $B_3H_7(CH_3BeH)_2Be(CH_3)_2BH_3$  and  $B_3H_7(CH_3BeH)_4BH_2CH_3$  (0.0266-gram sample) were as follows. Found were: Be, 0.57 matom; B, 0.63 matom;  $H_2$ , 2.25 moles;  $CH_4$ , 0.62 mmole; and B-alkyl  $CH_4$ , 0.10 mmole. Calculated were: Be, 0.61 matom; B, 0.68 matom;  $H_2$ , 2.30 mmoles;  $CH_4$ , 0.68 mmole; and B-alkyl  $CH_4$ , 0.10 mmole.

$Be(C_2H_5)_2$  and  $B_4H_{10}$  Reaction

- (C)  $Be(C_2H_5)_2$  (0.841 gram, 12.5 mmoles) was treated with  $B_4H_{10}$  (6.9 mmoles) at ambient temperature. After 18 hours, a solid-liquid mixture had formed in the reactor. Approximately 24 hours after initiation of the reaction, the mixture reverted to a clear liquid. The reactor was opened and hydrogen (2.03 mmoles) was removed. The volatile products were then removed and identified as being primarily  $[(C_2H_5)_2BH]_2$  (0.305 gram; vapor pressure, 3 mm Hg at 0 C). The nonvolatile material consisted of a very thick liquid which was extracted with n-hexane. This treatment resulted in the separation of the viscous material into an insoluble solid and an n-hexane soluble product. Concentration of the n-hexane afforded the isolation of the liquid product  $B_3H_7(C_2H_5BeH)BeH_2BH_3$ .
- (C) Analyses for  $B_3H_7(C_2H_5BeH)BeH_2BH_3$  (0.0350-gram sample) were as follows. Calculated (in mmoles) were: Be, 0.68; B, 1.35; hydridic hydrogen, 4.73; and hydrolyzable  $C_2H_5$  groups, 0.34. Found were: Be, 0.63; B, 1.38; hydridic hydrogen, 4.42; and hydrolyzable  $C_2H_5$  groups, 0.30.

Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>/B<sub>2</sub>H<sub>6</sub> Reaction

- (C) The first reaction was carried out by condensing B<sub>2</sub>H<sub>6</sub> (4.08 mmoles) into a reactor containing the diethyl beryllium (0.3400 gram, 5.1 mmoles). After 15.5 hours at ambient temperature, the reaction products consisted of a solid-liquid mixture. Removal and fractionation of the volatile materials yielded (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>B<sub>2</sub>H<sub>4</sub> (1.68 mmoles), B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (0.72 mmole, and Be(BH<sub>4</sub>)<sub>2</sub> (1.87 mmoles). A sample (0.0270 gram) of the nonvolatile solid recovered (0.1946) when hydrolyzed yielded H<sub>2</sub> (1.23 mmoles), C<sub>2</sub>H<sub>6</sub> (0.01 mmole), Be (0.50 matom, and B (0.18 matom), indicating that the solid was essentially (BeH<sub>2</sub>)<sub>6</sub> · [B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>.
- (C) The second reaction utilized a larger Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>/B<sub>2</sub>H<sub>6</sub> mole ratio (3.78/1.42). The reaction was halted after 18 hours. The reaction products were B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (1.74 mmoles), Be(BH<sub>4</sub>)<sub>2</sub> (0.33 mmole), and a nonvolatile solid (0.0894 gram). A sample (0.0224 gram) of the nonvolatile solid when hydrolyzed yielded H<sub>2</sub> (1.69 mmoles), C<sub>2</sub>H<sub>6</sub> (0.06 mmole), Be (0.71 matom), and B (0.16 matom) indicating again the formation of a boron alkyl-terminated beryllium hydride.

Be(BH<sub>4</sub>)<sub>2</sub>/Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> Reaction

- (C) Beryllium borohydride (1.382 grams, 35.8 mmoles) was added to a reactor containing Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (2.954 grams, 44.0 mmoles). The mixture became homogeneous after 0.5 hour at ambient temperature. Continued mixing resulted in the formation of a solid-liquid mixture from which B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (amount not measured) and an unknown were distilled. Isolation of the unknown from B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> was accomplished by fractional condensation at 11, -45, and -196 C; the unknown was retained by the -45 C cooled trap. The liquid exhibited a vapor pressure of 2 mm Hg at 25 C and analyzed as C<sub>2</sub>H<sub>5</sub>BH<sub>2</sub>BeH<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>BeH)BH<sub>3</sub>. Found (0.0793 gram sample) in mmoles were. Be, 1.30; B, 1.45; hydridic hydrogen, 6.0; and hydrolyzable C<sub>2</sub>H<sub>5</sub> groups, 0.82. Calculated in mmoles were: Be, 1.50; B, 1.50; hydridic hydrogen, 6.0; and hydrolyzable C<sub>2</sub>H<sub>5</sub> groups 0.75.

Reaction of  $\text{Be}(\text{C}_2\text{H}_5)_2$  and Tetraethyldiborane

- (C) Simple Mixing. A 2:1 mixture of the reactants was prepared by condensing at  $-196^\circ\text{C}$ , tetraethyldiborane (0.2985 gram, admixed with 5 weight percent of triethyldiborane by analysis) into a tube reactor containing the beryllium alkyl (1.06 mmoles). The mixture was then warmed to ambient temperature while stirring. After equilibrating the mixture for 72 hours, the entire sample was hydrolyzed. Mass spectrometric analyses of the gases collected (4.56 mmoles) indicated the composition to be 99.9 mole percent  $\text{H}_2$  and 0.1 mole percent  $\text{C}_2\text{H}_6$ . The quantity of hydrogen collected was in agreement with that expected (4.45 mmoles) based on analysis of the tetraethyldiborane. The absence of ethane in any appreciable quantities illustrated the near-quantitative hydriding of the beryllium.
- (C) Attempted Isolation of  $\text{BeH}_2[\text{BH}(\text{C}_2\text{H}_5)_2]_2$ . An aliquot of the tetraethyldiborane (0.4803 gram) used previously and  $\text{Be}(\text{C}_2\text{H}_5)_2$  (1.71 mmoles) were mixed in the manner described above. The reactor containing a clear liquid was cooled to  $0^\circ\text{C}$  after a reaction time of 72 hours at ambient temperature. The materials volatile at  $0^\circ\text{C}$  were removed from the reactor during 9 hours leaving a clear glass. The entire volatile (0.5411 gram) and nonvolatile (0.0540 gram) fractions were separately hydrolyzed to yield the following results. The volatile fraction contained: Be, 0.79 matom; B, 7.37 matoms; hydridic hydrogen, 4.62 mmoles; and hydrolyzable  $\text{C}_2\text{H}_5$  groups, 0.38 mmole. The nonvolatile fraction contained: Be, 0.79 matom; B, 0.23 matom; hydridic hydrogen, 2.44 mmoles; and hydrolyzable  $\text{C}_2\text{H}_5$  groups, 0.09 mmole.
- (C) A third experiment in which  $\text{Be}(\text{C}_2\text{H}_5)_2$  (1.65 mmoles) was added in the liquid state to  $[\text{BH}(\text{C}_2\text{H}_5)_2]_2$  (0.4900 gram), maintained at ambient temperature, yielded similar results. The volatile (0.5400 gram) and nonvolatile (0.1385 gram) fractions were separated as during the preceding experiment. Hydrolysis of the entire samples and analyses of the hydrolysate yielded the following results. Volatile fraction: Be, 0.80 matom; B, 7.01 matoms; hydridic hydrogen, 5.86 mmoles; hydrolyzable  $\text{C}_2\text{H}_5$  groups, 0.06 mmole;

nonvolatile fraction: Be, 0.65 matom; B, 0.48 matom; hydridic hydrogen, 2.22 mmoles; hydrolyzable  $C_2H_5$  groups, 0.01 mmole.

$B_4H_{10}/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$  Reaction

- (C) The copolymer  $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$  (0.7369 gram, 7.50 matoms of Be) was treated with  $B_4H_{10}$  (4.82 mmoles) for 94 hours. The volatile products were  $H_2$  (1.43 mmoles) and  $B(C_2H_5)_3$  (2.31 mmoles);  $B_4H_{10}$  (0.53 mmole) was also recovered. The nonvolatile liquid product was treated with an additional quantity of  $B_4H_{10}$  (1.54 mmoles) for 23 hours, after which time  $H_2$  (0.23 mmole),  $B_4H_{10}$  (0.70 mmole) and  $B(C_2H_5)_3$  (0.32 mmole) were recovered. The nonvolatile liquid product, containing a small amount of suspended solid, was extracted with n-hexane, filtered, and the n-hexane filtrate concentrated. The amount of liquid recovered was 0.5338 gram.
- (C) Analysis of a sample (0.0352 gram) of the liquid yielded  $H_2$  (2.85 mmoles), B (0.0085 gram, 0.79 matom), Be (0.0061 gram, 0.68 matom), and hydrolyzable  $C_2H_5$  groups, as ethane, (0.54 mmole). This results in Be:B:H: $C_2H_5$  ratios of 5.0:5.8:21.0:4.0; calculated for  $(B_3H_7)_2(C_2H_5BeH)_4BeH_2$  are: 5:6:22:4.

$B_4H_{10}/B_2H_6/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$  Reaction

- (C) Treatment of a  $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$  sample (0.6707 gram, 12.2 matoms of Be) with a mixture of  $B_4H_{10}$  (5.31 mmoles) and  $B_2H_6$  (1.45 mmoles) resulted in liquefaction of the copolymer in less than 48 hours. The volatile products were  $H_2$  (1.42 mmoles) and  $B(C_2H_5)_3$  (3.08 mmoles);  $B_4H_{10}$  (1.07 mmoles) was also recovered. The liquid product when extracted with n-hexane precipitated a quantity of solid. The filtrate after concentration yielded a clear mobile liquid weighing 0.1253 gram.
- (C) Analyses of a sample (0.0214 gram) of the liquid yielded  $H_2$  (1.95 mmoles), B (0.0064 gram, 0.59 matom), Be (0.0034 gram, 0.38 matom), and hydrolyzable

$C_2H_5$  groups, as ethane, (0.29 mmole). This results in Be:B:H: $C_2H_5$  ratios of 3.93:6.09:20.2:3.00; calculated for  $(B_5H_7)_2(C_2H_5BeH)_3$  are: 3:6:21:3.

$C_2H_5BeH/B_4H_{10}$  Reaction

- (C) A toluene solution of  $(C_2H_5BeH)_x$  was prepared by reacting  $(BeH_2)_x[B(C_2H_5)_3]_2$  (0.189 gram, 11 mmoles of  $BeH_2$ ) with  $Be(C_2H_5)_2$  (0.752 gram, 11.2 mmoles) in  $CaH_2$ -dried toluene (25 milliliters) at 50 C. After 72 hours, the small amount of remaining insoluble material was removed by filtration. A 2-milliliter aliquot of the filtrate was hydrolyzed yielding  $H_2$  (2.41 mmoles)  $C_2H_6$  (2.55 mmoles), and Be (22.9 mg, 2.54 atoms). The concentration of  $(C_2H_5BeH)_x$  in toluene (1.2 mmoles/milliliter) was calculated from these data.
- (C)  $B_4H_{10}$  (1.74 mmoles) was added to an aliquot of the toluene solution (4 milliliters, 4.8 mmoles of  $C_2H_5BeH$ ). An immediate reaction occurred between the two reagents resulting in the deposition of solids. Filtration and concentration of the filtrate by vacuum distillation at ambient temperature resulted in no nonvolatile liquid products.

$B_4H_{10}/B_2H_6/(CH_3BeH)_x$  Reaction

- (C) The  $(CH_3BeH)_x$  used during this experiment was prepared from  $Be(CH_3)_2$  and metathetical  $(BeH_2)_x$  (Ref. 8). End group analyses (boron analyses) of the synthesized alkylberyllium hydride, coupled with those for Be, hydridic hydrogen, and hydrolyzable  $CH_3$  (measured as  $CH_4$ ), indicated the composition  $[CH_3BeH]_{21}[Be(CH_3)_2]_5[B(C_2H_5)_3]_2$ .
- (C) A sample of the preceding compound (0.3858 gram, 11.0 atoms of Be) was treated with a mixture of  $B_4H_{10}$  (5.15 mmoles) and  $B_2H_6$  (2.20 mmoles). During 3 hours at ambient temperature, the glassy alkylberyllium hydride was converted to a mobile liquid. Materials volatile at ambient temperature were  $H_2$  (0.11 mmole),  $B_2H_6$  (0.01 mmole),  $B(CH_3)_3$  (0.16 mmole), unreacted  $B_4H_{10}$  (4.8 mmoles), and  $(CH_3BeH)_2$  (2.01 mmoles).

- (C) The residual liquid was analyzed using the sequential HCl/propionic acid procedure. The amounts of each constituent found and those values calculated for a 48:50 mixture (0.0277-gram sample) of  $B_3H_7(CH_3BeH)_5[Be(CH_3)_2]-B_3H_7$  and  $B_3H_7(CH_3BeH)_6[Be(CH_3)_2]BH(CH_3)_2$  were as follows. Found were: Be, 0.68 matom; B, 0.42 matom;  $H_2$ , 1.87 mmole;  $CH_4$ , 0.79 mmole; and B-alkyl  $CH_4$ , 0.11 mmole. Calculated were: Be, 0.68 matom; B, 0.42 matom;  $H_2$ , 1.86 mmole;  $CH_4$ , 0.78 mmole; and B-alkyl  $CH_4$ , 0.11 mmole.
- (C) A sample of the above liquid mixture (0.0528 gram) was treated with additional  $B_4H_{10}$  (1.16 mmole) and  $B_2H_6$  (0.12 mmole) at ambient temperature for 2.5 hours. The excess boranes and volatile products were removed but not identified. Analyses of the residual liquid (sample size, 0.0262 gram), using aqueous HCl only, satisfied the composition  $B_3H_7(CH_3BeH)_6BH_2CH_3$ . Found were: Be, 0.70 matom; B, 0.46 matom;  $H_2$ , 1.86 mmole; and  $CH_4$ , 0.71 mmole. Calculated were: Be, 0.69 matom; B, 0.46 matom;  $H_2$ , 1.85 mmole; and  $CH_4$ , 0.71 mmole.

$B_4H_{10}/(BeH_2)_x$  Reaction

- (C) Tetraborane (4.95 mmole) was added to a reactor containing boron alkyl-terminated  $BeH_2$  (0.0785 gram, 65.1 percent purity, 4.6 mmole of  $BeH_2$ ). After a reaction time of 4 days, hydrogen (2.45 mmole), unreacted  $B_4H_{10}$  (1.80 mmole),  $B_2H_6$  (0.09 mmole),  $Be(BH_4)_2$  (0.0347 gram, 0.9 mmole), and trace amounts of ethyldiboranes were recovered.

1,2-Trimethylenediborane/ $BeH_2$  Reaction

- (U) The preparation of 1,2-trimethylenediborane was carried out according to the procedure of Lindner and Onak (Ref. 12). The vapor-phase hydroboration of allene was performed in a circulating system (3.5-liter volume) containing  $C_3H_6$  (64 millimeters),  $B_2H_6$  (181 millimeters), and He (275 millimeters). The mixture was circulated through a heated (92 to 93 C) reaction zone until the total pressure in the system reached a constant value. The reaction products were continuously trapped at -78 C, and the diborane



derivative separated from the excess  $B_2H_6$  by fractional condensation at  $-97^\circ C$ . Infrared and hydrolytic analyses of the product indicated a mixture of 1,2-trimethylenediborane (70 percent) and n-propyldiborane (30 percent). This mixture was used without further purification.

- (C) An analyzed sample of  $(BeH_2)_x(BH_3)_2$  (0.0612 gram, 4.0  $\mu$ moles of  $BeH_2$ ) was treated at ambient temperature with the impure 1,2-trimethylenediborane (0.3076 gram, 3.15  $\mu$ moles). No apparent reaction occurred after 16 hours under these conditions. After 4 hours at  $57^\circ C$ , clumps of colorless needles,  $Be(BH_4)_2$ , formed above the hot zone. The total amount of volatile products weighed 0.0829 gram but were not further investigated because the nonvolatile product was a pasty solid.

#### PREPARATION OF ATEH LIQUIDS

##### Reaction of Beane With $Al(CH_3)_3$

- (C) The reactivity of Beane with  $Al(CH_3)_3$  at  $130^\circ C$  as a function of time was determined in the following manner. Six ampoules containing weighed amounts of Beane (96-percent purity) and commercial grade  $Al(CH_3)_3$  were sealed off in vacuo, and tumbled in an oil bath maintained at  $130^\circ C$ . After a specified time, the ampoule was removed from the oil bath, the ampoule was opened, and the unreacted Beane collected by filtration and carefully washed with n-hexane. After drying in vacuo, the weight of Beane recovered gave a measure of the extent of reaction with  $Al(CH_3)_3$  (Table 14).
- (C) The insoluble solid, remaining from the  $Al(CH_3)_3$ /Beane reaction, was identified in the following manner. A mixture of Beane (0.50 gram) and  $Al(CH_3)_3$  (10 milliliters) was heated, while stirring, at  $120^\circ C$  for 16 hours. The mixture was pressure filtered, and the solid was washed well with n-hexane. A sample (0.0203 gram) of the insoluble material recovered (0.2543 gram) was then analyzed for beryllium (1.69 atoms), hydridic hydrogen (3.80  $\mu$ moles) and aluminum ( $< 0.1$  mg). The recovered Beane, based on the beryllium result, was 92 percent pure.

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TABLE 14

## REACTION OF BEANE AND $\text{Al}(\text{CH}_3)_3$ AT 130 C

Heating Time, hours	Beane Used, milligrams*	$\text{Al}(\text{CH}_3)_3$ Used, milligrams	Beane Recovered, milligrams	Beane Reacted, percent
8	50.9	638.8	17.8	67.7
16	54.6	677.5	13.0	79.4
24	50.9	637.8	9.8	84.0
48	55.7	680.4	3.0	98.6
72	55.2	685.2	2.4	99.7

\*Purity of Beane, 96 weight percent

### Composition of ATBH Liquid vs Reaction Time

- (c) The n-hexane extracts from the preceding experiments were subjected to vacuum pumping until the loss in weight per hour was 2 to 3 milligrams. This resulted in the removal of the n-hexane as well as any unreacted  $\text{Al}(\text{CH}_3)_3$ . The analytical results obtained on the nonvolatile materials are presented in Table 15.

TABLE 15

## ANALYSES OF $\text{Al}(\text{CH}_3)_3$ /BEANE PRODUCTS

Heating Time, hours	Weight of Product, milligrams	Analyses, mole ratios			
		Al	Be	H	$\text{CH}_3$
8	113.7	2	6.5	9.3	10.5
16	131.8	2	5.5	8.4	8.6
24	160.1	2	5.7	9.1	8.8
48	152.7	2	6.6	11.6	9.4
72	168.5	2	6.6	10.4	8.5

A trend toward decreased methyl group and increased hydride contents with longer reaction time is indicated from these data.

Formation of Dimethylalane

- (C) The formation of dimethylalane as a byproduct of the  $\text{Al}(\text{CH}_3)_3$ /Beane system was investigated as follows. A mixture of Beane (0.033 gram, 96 percent purity, 2.9 mmoles) and commercial grade  $\text{Al}(\text{CH}_3)_3$  (0.350 gram, 4.9 mmoles) was heated for 24 hours at 120 C. The volatile materials (0.310 gram) were then removed by vacuum pumping. Analyses of the volatile materials in toto revealed Be:Al:CH<sub>3</sub>:H mole ratios of 1:20.9:59.7:8.1. These results agree favorably with those expected based on a mixture of  $\text{Al}(\text{CH}_3)_3$  (64.5 percent),  $(\text{CH}_3)_2\text{AlH}$  (33.5 percent), and  $\text{CH}_3\text{BeH}$  (2.0 percent) present in the form of a complex with either or both of the alanes.

Reaction of Beane and Dimethylalane

- (C) A mixture of Beane (0.0522 gram, 96 weight percent  $\text{BeH}_2$ , 4.55 mmoles) and dimethylalane (0.595 gram, containing 12 weight percent monomethylalane by analysis) was heated at 130 C for 24 hours. The mixture was then processed in the same manner used for the  $\text{Al}(\text{CH}_3)_3$  studies. Analysis of the filtrate showed the presence of 21.3 percent of the beryllium used. The liquid nonvolatile product (0.2075 gram) was quite viscous and had the Al/Be/H/CH<sub>3</sub> ratios of 2.0/0.68/2.99/4.08, indicating the presence of residual dimethylalane.

Hydriding of ATBH Liquids

- (C) A mixture of  $\text{Al}(\text{CH}_3)_3$  (104 mmoles) and Beane (45.4 mmoles) was heated at 120 C for 16 hours. The filtered solution was used as the standard ATBH liquid for the hydriding reactions. An aliquot (2 milliliters) of the filtrate was taken and the excess  $\text{Al}(\text{CH}_3)_3$  was removed until constant weight ( $0.120 \pm 0.002$  gram) was achieved. Analysis of the viscous residue gave the Be:H:CH<sub>3</sub> ratio of 1.0:1.0:1.85.

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- (C) B<sub>2</sub>H<sub>6</sub> Reaction. A 2-milliliter aliquot of the standard ATBH material was pumped to constant weight (0.1185 gram) and subsequently treated with B<sub>2</sub>H<sub>6</sub> (0.455 mmole) at ambient temperature. The mixture became quite mobile within a few minutes after reaching ambient temperatures. The volatile components (0.0588 gram) were fractionated to obtain B(CH<sub>3</sub>)<sub>3</sub> (0.06 mmole) and an aluminum-containing liquid. Analysis of the nonvolatile viscous material revealed the Be:H:CH<sub>3</sub> ratio of 1:1.5:0.93. The amount of aluminum (14.9 milligrams) found in the volatile fraction corresponded to a 80 percent displacement.
- (C) Be(BH<sub>4</sub>)<sub>2</sub> Reaction. A sample (0.1204 gram) of the ATBH material, as obtained above for the previous reaction, was treated with Be(BH<sub>4</sub>)<sub>2</sub> (0.0175 gram, 0.452 mmole) at ambient temperature. The viscous ATBH material became quite mobile and contained only a small quantity of solid after 1 hour; all but a trace of this material dissolved after stirring overnight. Fractional condensation yielded an aluminum-containing compound but no alkyl-boron derivatives. Analyses of the nonvolatile viscous material revealed the Be:H:CH<sub>3</sub> ratio of 1:1.8:0.92, while the volatile fraction contained 82 percent of the aluminum.
- (C) B<sub>4</sub>H<sub>10</sub> Reaction. A third sample (0.1213 gram) of the prepared ATBH liquid was treated with B<sub>4</sub>H<sub>10</sub> (0.429 mmole) at ambient temperature. The liquid required approximately 1 hour to become mobile. After stirring the mixture for 16 hours, the liquid products were separated into volatile and non-volatile fractions which were subsequently analyzed. The volatile portion contained approximately 85 percent of the aluminum while the nonvolatile liquid material had Be:H:CH<sub>3</sub> ratios of 1.0:2.9:1.0.

### Decomposition of Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> at Ambient Temperature

- (U) The precipitate formed during ambient temperature storage of Be(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was trituated under n-hexane, filtered, and washed copiously with the same hydrocarbon. The solid was then dried in vacuo for 30 minutes.

Analysis of a sample (0.0562 gram) of the solid revealed  $H_2$  (0.53 mmole), hydrolyzable  $C_2H_5$  groups (1.59 mmoles), and Be (1.0 matom). This resulted in Be: $C_2H_5$ :H ratios of 1.9:3.0:1.0; calculated for the monomeric unit  $(C_2H_5)_2Be \cdot C_2H_5BeH$  were: 2:3:1.

#### Pyrolysis of $Be(C_2H_5)_2$

- (U) In an attempt to prepare samples of the purported compound  $C(BeH_2BeC_2H_5)_4$  from the pyrolysis of  $Be(C_2H_5)_2$ , several runs were made at 200 C for varying time periods. A typical pyrolysis was conducted in the following manner to yield the indicated volatile species. A sample of  $Be(C_2H_5)_2$  (4.26 grams, 63.5 mmoles) was heated in a sealed flask for 1.5-hour intervals at temperatures up to 200 C for a total time of 16 hours. After this time period, the evolution of pyrolysis gases had ceased. The volatile products consisted of  $H_2$  (0.25 mmole),  $C_2H_6$  (19.6 mmoles),  $C_2H_4$  (1.2 mmoles), and 0.629 gram of a mixture of higher hydrocarbons; the higher hydrocarbons were identified by mass spectrometric analyses as propene, n-propane, 2-butene, n-butane, and pentanes.
- (U) Analytical data obtained on the crude yellow product from two different runs are presented in Table 16.

TABLE 16

#### ANALYSES OF CRUDE PYROLYSIS PRODUCT OF $Be(C_2H_5)_2$

Sample Size, mg	$H_2$ , mmoles	$CH_4$ , mmoles	$C_2H_6$ , mmoles	Be, matoms	Be:H: $C_2H_6$ : $CH_4$ Ratios	Material Balance, percent
139.2	2.39	0.39	1.28	2.92	8.0:6.5:3.5:1.1	51.6
91.8	1.50	0.22	0.82	1.68	8.0:7.1:3.9:1.1	47.7

- (U) Samples of the crude product were twice-distilled at 90 to 95 C ( $5 \times 10^{-4}$  mm Hg) in a Hickman Molecular Still. Distillation did not yield a material of high purity. Analytical data for distilled samples are presented in Table 17.

TABLE 17

ANALYSES OF DISTILLED PYROLYSIS

PRODUCT OF  $\text{Be}(\text{C}_2\text{H}_5)_2$

Expt. No.	Sample Size, mg.	$\text{H}_2$ , mmoles	$\text{CH}_4$ , mmoles	$\text{C}_2\text{H}_6$ , mmoles	Be, matoms	Be:H:C <sub>2</sub> H <sub>6</sub> :CH <sub>4</sub> Ratios	Material Balance Percent
1	66.3	1.58	0.22	0.84	1.54	8.0:8.2:4.4:1.1	65.1
2	51.7	1.09	0.26	0.98	1.31	8.0:6.7:6.0:1.4	87.6
3	60.6	1.52	0.23	0.77	1.55	8.0:7.9:4.0:1.2	68.2

- (U) A separate sample of the liquid from experiment No. 1 was treated with  $\text{D}_2\text{O}$  to determine if the diluent was chemically or physically bound in the mixture. After deuterolysis, the hydrolyzate was extracted with n-pentane, the n-pentane was removed, and the residual oil was examined by infrared spectroscopy for C-D absorptions. No absorptions attributable to C-D bonds were found.

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13. ABSTRACT Studies of liquid beryllium hydride synthesis have resulted in a number of new species with theoretical specific impulses approaching 330 seconds and further defined the most promising classes of this type of high-energy fuel. In general, it appears that terminators derived from higher borane fragments (e.g., $B_3H_7$ ) are more advantageous than simple $BH_3$ terminators. Liquids with $B_3H_7$ terminators exhibit high theoretical impulse and satisfactory fluidity, and unlike many $BH_3$ -terminated liquids, are not subject to reversible dissociation. The bulk of this investigation was concerned with the preparation of borane-terminated beryllium hydride (BTBH) liquids from the reaction of $B_4H_{10}$ with beryllium alkyls and alkylberyllium hydrides. The nature of the reaction products was dependent upon the experimental conditions. The use of a $B_4H_{10}/Be(CH_3)_2$ mole ratio of 0.5 and an extended reaction time yielded the best product, a liquid analyzing as $B_3H_7(CH_3BeH)_2BeH_2BH_3$ (specific impulse, 329 seconds with $H_2O_2$ ). The use of $B_2H_6/B_4H_{10}$ mixtures simplified the complex reactions involving pure $B_4H_{10}$ and solid beryllium compounds. Such mixtures increased the liquefaction rates of the beryllium compounds and also resulted in a significant decrease in the amount of $B_4H_{10}$ decomposition during its reactions. Ethyl-substituted BTBH liquids were synthesized. The compound $B_3H_7-(C_2H_5BeH)BeH_2BH_3$ (specific impulse, 326 seconds) remained fluid at $-40^\circ C$ . Conditions for the quantitative reaction of $Al(CH_3)_3$ and Beane were established for the preparation of alane-terminated beryllium hydride (ATBH) liquids. The displacement of the alane terminators from ATBH liquids by $B_2H_6$ , $B_4H_{10}$ , or $Be(BH_4)_2$ demonstrated the feasibility of employing AFRPL materials as precursors for BTBH liquids (C)		

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